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ABBREVIATIONS AND SYMBOLS

μg/g	Micrograms per gram
μg/L	Micrograms per liter
μL	Microliter
μM	Micromoles per liter
σ	Standard deviation
τ	Residence time (equation 1)
Al	Aluminum
ANOVA	Analysis of variances
As	Symbol for arsenic, except at the beginning of a sentence
As(III)	Sum of concentrations of H_3AsO_3 and $H_2AsO_3^-$
As(V)	Sum of concentrations of H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$, and AsO_4^{3-}
As_2O_3	Arsenic trioxide, arsenolite, claudetite
As_2S_3	Orpiment
C	Concentration (equation 1)
C_0	Initial concentration (equation 1)
DMAA	Dimethylarsinic acid
DO	Dissolved oxygen
Eh	Redox potential relative to the hydrogen electrode
FeAsS	Arsenopyrite
FeS_2	Pyrite
H_2S	Hydrogen sulfide
HFO	Hydrous ferric oxide
HPLC	High-performance liquid chromatography
IC	Ion chromatography
ICP-MS	Inductively coupled plasma-mass spectrometry
IEPA	Illinois Environmental Protection Agency
ISWS	Illinois State Water Survey
MCL	Maximum contaminant level
MDL	Method detection limit
mg	Milligram(s)
mg/L	Milligrams per liter
MMAA	Monomethylarsonic acid
mV	Millivolts
m/z	Ratio of mass to change
n	Number of samples
NH_3-N	Ammonia nitrogen
NPOC	Non-purgeable organic matter
OM	Organic matter
ORP	Oxidation-reduction potential
pKa	Negative logarithm of acid dissociation constant

ABBREVIATIONS (Concluded)

r^2	Correlation coefficient squared
Redox	Oxidation-reduction
t	Time (equation 1)
TCHD	Tazewell County Health Department
TOC	Total organic carbon (equivalent to NPOC in this study)
USEPA	United States Environmental Protection Agency
WMRC	Waste Management and Research Center

ABSTRACT

Groundwater samples were collected from approximately 50 private wells in Tazewell County, an area where arsenic contamination is known from previous sampling, and northwest Champaign County, an area for which very few arsenic data were available. Most of the wells were finished in the Mahomet Aquifer, with roughly equal numbers of wells near the bottom, middle, and upper part of the aquifer. A few of the wells were finished in the Glasford Aquifer, which lies above the Mahomet. A reliable, robust method for arsenic speciation was developed based on separation of species by HPLC and ICP-MS detection. The samples were analyzed for total arsenic, arsenic species, metals, anions, alkalinity, ammonium, and total organic carbon. In both counties wells with high arsenic concentrations were spread throughout the study area. In Champaign County, 40% of the wells had nondetectable (<1 μg/L) arsenic, 90% had less than the maximum contaminant level (MCL) of 10 μg/L, and one well had over 50 Ϝg/L. In Tazewell County, 25% of the wells had nondetectable arsenic, 55% had less than the MCL, and 10% had over 50 μg/L. In both counties the spatial distribution of arsenic was complex. Wells with high concentrations were often located less than one mile from wells with nondetectable arsenic. In Tazewell County, the percentages of wells with arsenic concentrations above the MCL were roughly equal in the shallow, intermediate, and deep parts of the Mahomet Aquifer. Although there were relatively few samples from the Glasford Aquifer, there appeared to be a higher percentage with arsenic concentrations above the MCL. In most samples As(III) made up over 90% of the dissolved arsenic and particulate arsenic (retained by a 0.45 μm filter) made up less than 10% of the total. The arsenic speciation was consistent with thermodynamic calculations based on the measured pH and oxidation-reduction potential values. Although there were no good correlations between arsenic and other analytes, high arsenic concentrations were associated with low sulfate concentrations and with high concentrations of bicarbonate, fluoride, and organic carbon.

Samples of raw groundwater and finished potable water were collected from 11 municipal water treatment plants that withdraw water from the Mahomet Aquifer. All facilities but one employed some form of iron removal and there was some arsenic removal at all of these facilities. There was no arsenic removal at the facility that did not remove iron. Two facilities had arsenic concentrations below the new MCL in their finished water. There was very little particulate arsenic in the raw water at all facilities. At two facilities the total (unfiltered) arsenic concentration was above the MCL but the dissolved (filtered) concentration was below the new MCL. Improved filtration may enable these facilities to satisfy the new MCL. As in the private wells, As(III) was the predominant arsenic species in the raw waters at all facilities. As(V) was the predominant species in treated waters because of chlorination.

INTRODUCTION

Study Objectives

The Mahomet Aquifer in central Illinois is the source of drinking water for many communities and thousands of private homes (Figure 1). Naturally occurring arsenic (As), a suspected carcinogen, has been found in many areas of the aquifer at concentrations greater than 10 Ｆg/L. In 2001, the U.S. Environmental Protection Agency (USEPA) announced that the maximum contaminant level (MCL) for arsenic would be lowered from 50 to 10 Ｆg/L, with final implementation in 2006. Existing data regarding the levels of arsenic are limited, especially for private wells. Some recent research (WARNER, 2001) has suggested that arsenic concentrations increase with depth, but not all of the available data support this hypothesis. Therefore, one of the objectives of this study was to characterize the distribution of arsenic in the aquifer to evaluate the potential links between levels of arsenic in the aquifer and the relationship with the bedrock below the aquifer as well as the confining layer overlying the aquifer.

Arsenic in groundwater occurs in two chemical forms, or species, As(III) and As(V). The chemical and toxicological properties of the two species are quite different and the removal efficiencies for each may be somewhat different. The determination of arsenic speciation is a difficult task and few prior data are available. Therefore, a second goal of this study was to characterize the arsenic speciation in samples from both private wells and community wells to evaluate the predominance of each species in the aquifer and determine if and how conventional treatment affects arsenic speciation.

Water treatment plants remove some arsenic in conventional processes, such as iron (Fe) removal and softening, but these processes are not optimized for arsenic removal. Substantial data exist regarding arsenic levels in community water supplies, especially treated samples. However, data on both raw and treated samples for a given system are not as readily available. Clearly, understanding the removal efficiency of existing systems will be an important component for proper application of treatment methods. Therefore, an additional objective of this research was to determine the current arsenic-removal efficiency of some community water treatment plants that draw water from the Mahomet Aquifer. By determining the types of treatments and chemical conditions that promote the removal of arsenic using conventional treatment, public water supplies may be able to use these results to improve their arsenic removal.

Background

Arsenic Toxicity
Arsenic is well known for its acute toxicity. For example, an ingested dose of 70-180 mg of arsenic trioxide (As_2O_3) is lethal to humans (LEONARD, 1991). Somewhat lower doses produce sub-acute effects in the respiratory, gastrointestinal, cardiovascular, and nervous systems (JAIN and ALI, 2000). Chronic exposure to arsenic in drinking water has been linked to serious dermatological conditions, including blackfoot disease (LU et al., 1991). Epidemiological studies have linked arsenic in drinking water with cancer of the skin, bladder, lung, liver, and kidney (HINDMARSH, 2000) and other ailments (KARIM, 2000). Both As(III) and As(V) are strongly

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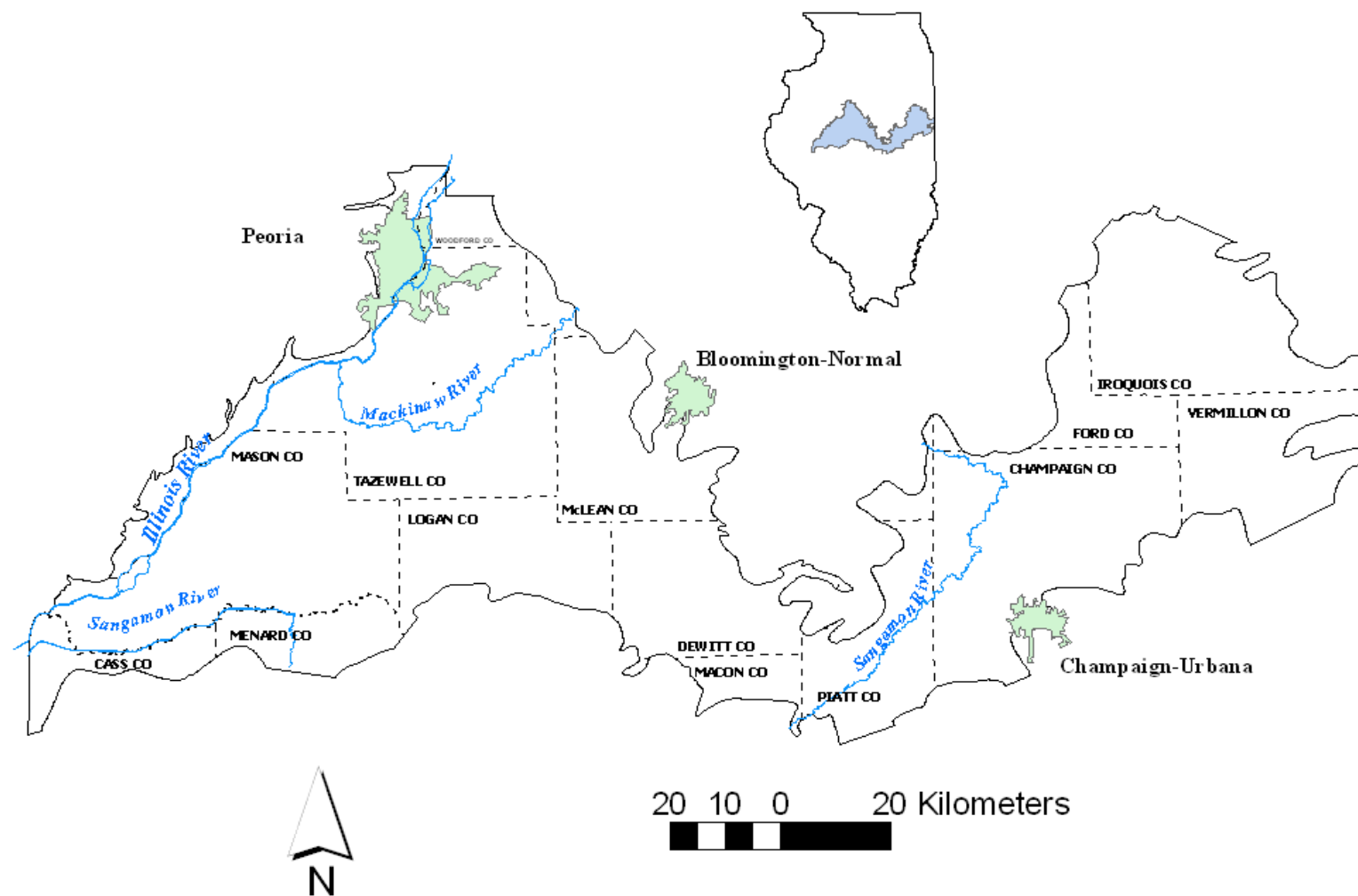
Figure 1. Map of the Mahomet Aquifer in Illinois.

adsorbed in the human body (HINDMARSH and MCCURDY, 1986). As(III) tends to accumulate in the tissues, whereas As(V) and organic arsenic are rapidly and almost completely eliminated via the kidneys (BERTOLERO et al., 1987). The MCL for arsenic in drinking water for many years was 50 Ғg/L, but recent research (SMITH et al., 1992) has suggested that the cancer risk at 50 Ғg/L is unacceptably high. A review of the available arsenic- and health-related data prompted the USEPA to lower the MCL to 10 Ғg/L, the same as the World Health Organization's standard.

Arsenic Occurrence in Groundwater

Arsenic is a minor constituent of some common minerals, and dissolved arsenic concentrations greater than 1 Ғg/L are common in groundwater. In some aquifers and under certain conditions, much greater arsenic concentrations can be found, and concentrations above 10 Ғg/L are not uncommon. FOCAZIO ET AL. (2000) reviewed analyses of 2,262 public groundwater supply sources and WELCH ET AL. (2000) reviewed analyses of 30,000 groundwater samples from throughout the United States and found that for about 8% and 10% of them, respectively, arsenic concentrations were greater than 10 Ғg/L. A statewide survey of Illinois Environmental Protection Agency (IEPA) records of ambient water quality from 347 Illinois community groundwater supplies in the 1990s found that 77 (22%) had at least one sample with arsenic greater than 10 Ғg/L (NRDC, 2000). FOCAZIO ET AL. (2000) reported that the median arsenic concentration for all groundwater samples from Illinois was 1 Ғg/L.

Hydrogeology of The Mahomet Aquifer

The Mahomet Aquifer is one of the largest and most important aquifers in Illinois, providing approximately 670,000 people in central Illinois with drinking water. The Mahomet Aquifer is an unconsolidated sand and gravel aquifer that is contained in the buried Mahomet Bedrock Valley that extends across central Illinois from Indiana to the Illinois River. The aquifer is mostly overlain by thick layers of glacial till with interbedded sand layers that are also used for water supply. The bedrock formations underlying the Mahomet Aquifer can be divided into two regions based upon the mapping by WILLMAN (1967). West of the Champaign-Piatt County line are Pennsylvanian shales with interbedded sandstones, limestones, and coals while east of this line are thick Silurian dolomites and a variety of Devonian and Mississippian sedimentary rocks.

Three major episodes of glaciation deposited sediments in the Mahomet Valley. The oldest and lowermost unit is the pre-Illinoian Banner Formation, which was generally deposited on the bedrock surface. The Mahomet Sand comprises the lower portion of this formation and fills the deepest parts of the valley with up to 150 feet of outwash sand. The lower Mahomet Sands were derived from glaciers that came from the east, while upper Mahomet Sands were derived from glaciers that came from the north (MANOS, 1960). KEMPTON ET AL. (1991) describe the Mahomet Sand as coarse, gravelly sands that tend to be finer in the upper portions of the unit. The upper portions of the Banner Formation include two till (diamicton) units, the Hillery and Tilton Members. Basal sands are associated with the Tilton Member.

The Illinoian-age Glasford Formation overlies the Banner Formation except in Mason and western Tazewell Counties where it either was not deposited or has been eroded off. The Glasford Formation consists of two till layers, the Vandalia Member and the overlying Radnor Member. Both members have associated basal sand layers that are discontinuous and generally

less than 25 feet thick. Even so, these sands are an important source of water for domestic wells. The two Glasford sands can provide an important source of water to the Mahomet Aquifer where they are connected to the Mahomet Sand. These connections have been found in Tazewell, McLean, Piatt, Champaign, and Vermilion Counties. The Wisconsinan-age Wedron Group overlies the Glasford Formation and is surficial material in most of the study area. This group consists mainly of two till units, the Tiskilwa Member and the overlying Lemont Member. Thin lenses of sand and gravel are locally present but are not adequate for development of a water supply other than for domestic wells. The Wisconsinan glaciers terminated in Tazewell and Logan counties, forming the Shelbyville terminal moraine.

Groundwater flow in the Mahomet Aquifer before development was from east to west, with groundwater discharging to the Illinois, Mackinaw, and Sangamon Rivers. But now, because of groundwater pumpage, the groundwater flow is divided into three main flow cells. The highest water levels occur near Paxton in Ford County with flow radiating away south and west into Champaign County, north into Iroquois County, and east into Vermilion County. In Champaign County, a large cone of depression has formed due to the annual withdrawals of roughly 18 million gallons per day from the well field that provides Champaign, Urbana, and several surrounding communities with drinking water. This cone of depression has caused a reversal of flow in the aquifer west of the well field so that flow is east toward the well field. The cone of depression extends into Piatt County, where it forms a groundwater divide that stretches across the valley. This divide occurs near where the aquifer is believed to be connected to the Sangamon River (ROADCAP and WILSON, 2001). West of Piatt County groundwater flow is to the west through Dewitt, McLean, Tazewell, Logan, and Mason Counties, with the Illinois, Mackinaw, and Sangamon Rivers the principal discharge areas.

In the Tazewell County region, groundwater flow in the Mahomet Aquifer "splits", with some of the flow going west into Mason County, discharging into the Mackinaw and Sangamon Rivers, and the rest of the flow going north into the Mackinaw Bedrock Valley and ultimately discharging into the Illinois River. This groundwater divide coincides with a bedrock high that pinches off the Mahomet Aquifer and separates the flow in the aquifer as the Mahomet and Mackinaw bedrock valleys come together in Tazewell and McLean Counties. The divide runs from southeast to northwest from roughly McLean to Tremont. A second bedrock high near Tremont also pinches off the aquifer, causing groundwater to flow around it.

Arsenic in the Mahomet Aquifer

Existing sources of arsenic data for the Mahomet and overlying aquifers are given in Table 1. The IEPA Municipal Ambient Water Quality Database contains samples collected from over 100 public water supplies that get their drinking water from the Mahomet Aquifer. The data are from approximately 1980 to the present. The Illinois State Water Survey (ISWS) Water Quality Database contains samples from both private (approximately 1900 to the present) and public wells (primarily prior to 1980). There also have been investigations by the ISWS and other agencies that have included analysis for arsenic in samples from the Mahomet and overlying aquifers (HOLM, 1995; HOLM and CURTISS, 1989; RAY and KELLY, 1999; WARNER, 2001). The Tazewell County Health Department (TCHD) analyzed samples for many homeowners in 1985-1986 in response to concerns over arsenic in well water. Kelly and Wilson (unpublished data,

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Table 1. Sources of aqueous arsenic data in the Mahomet Aquifer, Illinois			
Study or Database	*Location in Aquifer*	*# of wells*	*Well type*
IEPA/ISWS Databases	Entire Aquifer	460	Public
Tazewell Co. Health Dept.	SE Tazewell Co. (Western)	494	Private
HOLM and CURTISS (1988)	Entire Aquifer	19[*]	Public
HOLM and CURTISS (1988)	SE Tazewell Co. (Western)	20	Private
HOLM (1995)	Western	33	Monitoring
KELLY and RAY (1999)	Central Mason Co.	5[†]	Monitoring
WARNER (2001)	Eastern and Central	30	Private
KELLY and WILSON (2000; 2002)	Central	39	Private

[*] Wells selected due to elevated arsenic levels
[†] Multi-port wells with between 8 and 11 ports at different depths.

ISWS) collected groundwater samples for arsenic analysis from private wells in DeWitt, Macon, and Piatt Counties in 2000 and 2002.

A summary of the arsenic concentrations found in the IEPA and ISWS databases and by previous investigations is shown in Table 2. Arsenic has been found in groundwater from many parts of the Mahomet Aquifer with higher concentrations generally in the western part of the aquifer (McLean, Logan, and Tazewell Counties) (PANNO et al., 1994). In the mid-1980s, samples from 590 private wells, mainly in the southeast part of Tazewell County, were submitted to the TCHD for arsenic analysis (Figure 2). Approximately 34% and 59% had arsenic concentrations at or above 50 and 10 Ⅎg/L, respectively. These percentages are much greater than those found for community wells in the area. It should be noted that there is no well depth information from the TCHD investigation, and many of these samples may have come from aquifers overlying the Mahomet Aquifer. HOLM (1995) found that the shallower aquifers in the western part of the Mahomet Valley (Tazewell, McLean, and Logan Counties) had a higher percentage of samples with high arsenic concentrations, compared to the Mahomet Aquifer. The spatial distribution of arsenic in the western part of the Mahomet Aquifer is complex. For example, arsenic concentrations below 3 Ⅎg/L were found less than one mile from concentrations greater than 90 Ⅎg/L (HOLM, 1995).

Kelly and Wilson (unpublished data, ISWS, 2000 and 2002) also sampled 39 wells in the central part of the Mahomet Aquifer (Piatt, DeWitt, and Macon Counties). The sampled wells were selected to be in the deep part of the aquifer and along the buried valley walls. The lowest arsenic concentrations tended to be in the central (thalweg) part of the aquifer, with greater concentrations closer to the valley walls (Figure 3). The valley walls had relatively high concentrations of sodium (Na) and chloride (Cl^-), while sulfate (SO_4^{2-}) was absent. It has been hypothesized that in this area there is recharge of highly mineralized water to the Mahomet Aquifer from bedrock sources along the valley walls (PANNO et al., 1994).
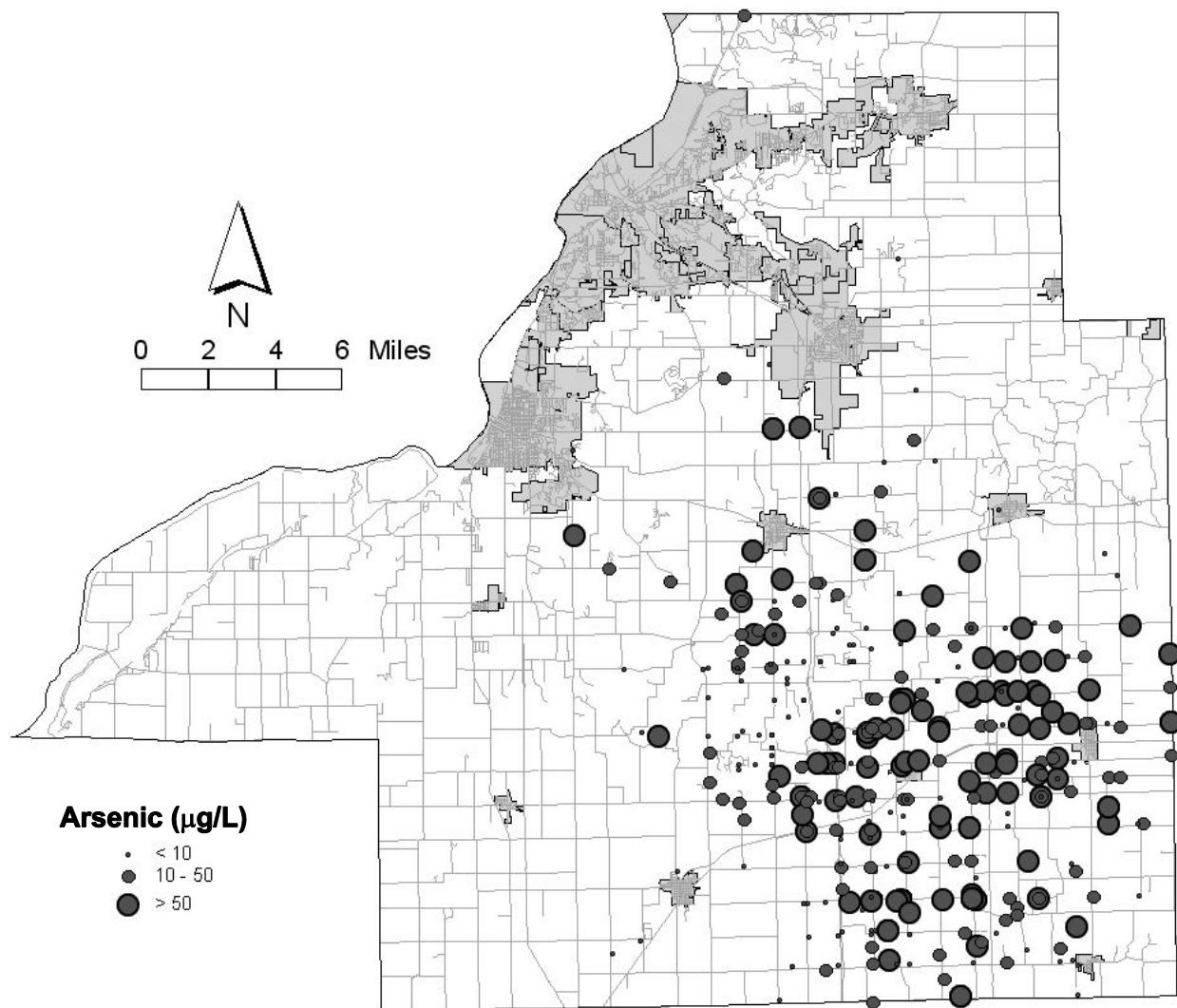
Figure 2. Arsenic concentrations in well water samples submitted to
the Tazewell County Health Department in 1985-1986.
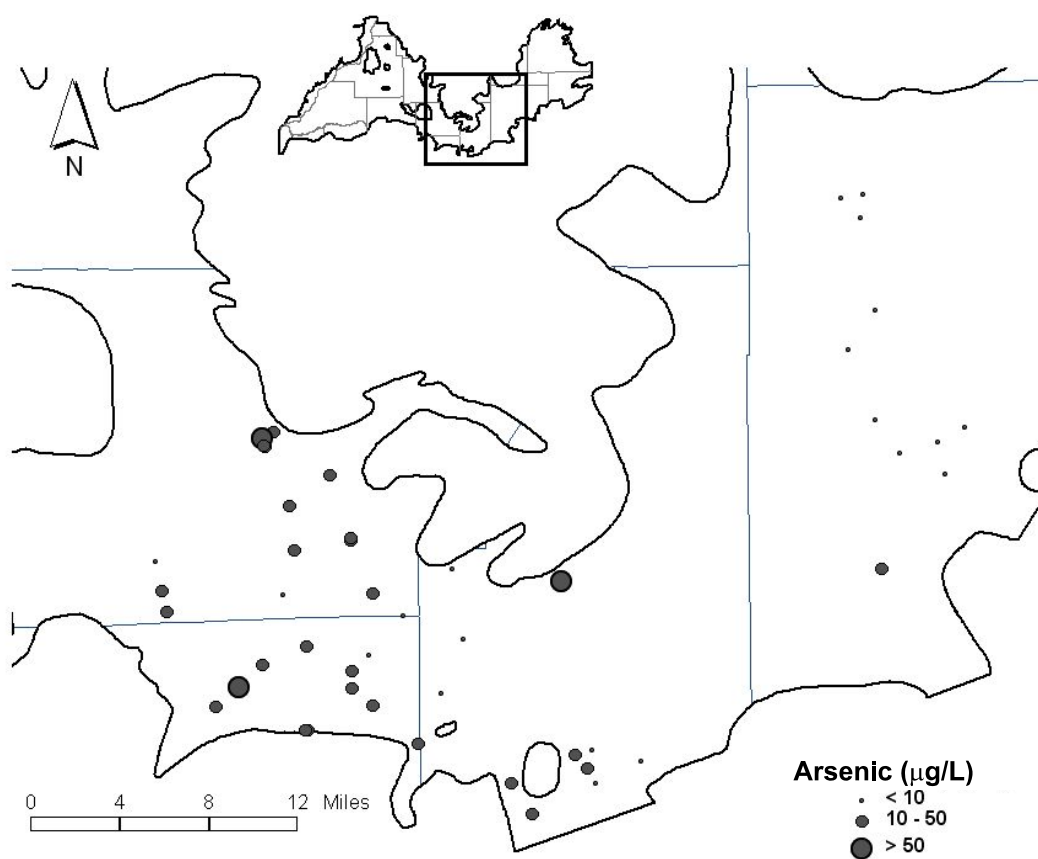
Figure 3. Arsenic concentrations of private wells from the deep Mahomet Aquifer in Piatt, DeWitt, and Macon Counties sampled by Kelly and Wilson (unpublished data, 2000 and 2002) and in Champaign County sampled in this study. The heavy solid lines indicate Mahomet Aquifer bedrock valley walls and bedrock highs.

Table 2. Arsenic concentrations from published data sets and studies in the Mahomet Aquifer. Concentrations in Ϝg/L; ND = not determined.								
					% of samples in conc. range			
Study	*n*	*min*	*max*	*median*	*#10*	*10-20*	*20-50*	*>50*
IEPA (1980-1999)	460	<1	135	2	68.8	11.9	13.7	5.6
HOLM and CURTISS (1988): public	19	<1	80	46	42.1	5.3	21.1	31.6
TCHD (1985-1986)	494	<1	259	26	39.3	6.9	18.6	35.2
HOLM and CURTISS (1988): private	20	9	226	42	10.0	5.0	45.0	40.0
HOLM (1995)	33	<3	99	9	54.6	21.2	18.2	6.1
KELLY and RAY (1999)	134	<50	<50	<50	ND	ND	ND	0.0
WARNER (2001)	30	<1	84	17	56.7	3.3	33.3	6.7
KELLY and WILSON (2000; 2002)	39	0.8	266	19	28.2	25.6	38.4	7.7

The median arsenic concentrations of community wells in the Mahomet Aquifer and overlying aquifers were obtained from the IEPA database and plotted on a location map (Figure 4). Arsenic concentrations tended to be greater in the central and west-central areas, although high and low concentrations were found in all areas. There were very few wells with concentrations greater than 50 Ϝg/L; several appeared to be located near the valley walls, as Kelly and Wilson (unpublished data, ISWS, 2000 and 2002) found, suggesting an influx of arsenic from bedrock sources. In most counties, there was no apparent correlation between arsenic concentrations and depth, although in DeWitt and Mason Counties arsenic concentrations seem to increase with depth (Figure 5).

Glacial tills are known to contain arsenic-bearing materials and because these tills typically overlie the sand-and-gravel aquifer, they may be a source of the arsenic. The tills are derived largely from the regional bedrock, thus any arsenic bearing minerals in the bedrock would also be found in the till. These minerals may have been weathered and oxidized during deposition. WARNER (2001) analyzed 18 samples from cores taken to bedrock; five of the cores were taken from an area of high arsenic concentrations. WARNER (2001) did not find elevated arsenic levels in the solid phases. The overlying tills and underlying bedrock had greater levels of arsenic than the sand and gravel, but the greatest concentration was only 21 Ϝg/g, found in Pennsylvanian shale bedrock.

Geochemistry of Arsenic in Groundwater
Arsenic in groundwater occurs in two oxidation states, As(III) (arsenite) and As(V) (arsenate). As(III) is usually present in solution as $As(OH)_3E$, while As(V) usually exists as an oxyanion, $H_2AsO_4^-$ or $HAsO_4^{2-}$ ($pK_a = 6.98$). As(III), the more reduced form, is more toxic than As(V) and also more mobile under most geochemical conditions. Although methylated forms of arsenic are sometimes found in surface waters, they have only rarely been found in groundwater (CHATTERJEE et al., 1995; IRGOLIC, 1982), except in cases of gross contamination by herbicides (HOLM et al., 1979). SHRAIM ET AL. (2002) did find low concentrations (< 2 μg/L) of methylated species in groundwater from West Bengal, although the inorganic arsenic concentration in those samples was extremely high (> 300 μg/L).
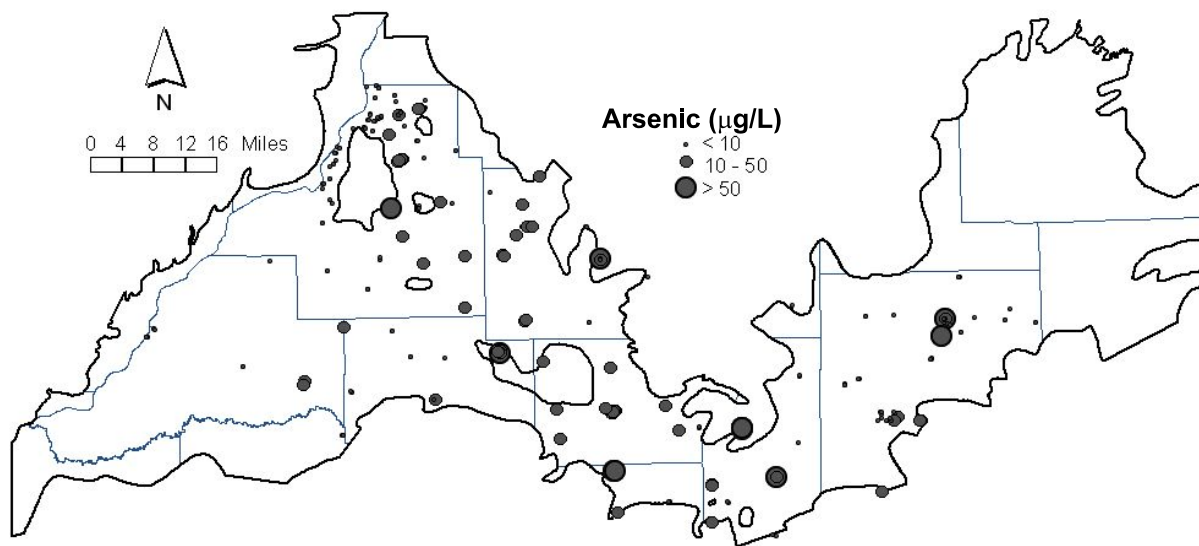
Figure 4. Median arsenic concentrations of community wells in the Mahomet and overlying aquifers west of and including Champaign County. Data are from the IEPA ambient groundwater database, 1980-1999. Heavy solid lines indicate Mahomet Aquifer bedrock valley walls and bedrock highs.
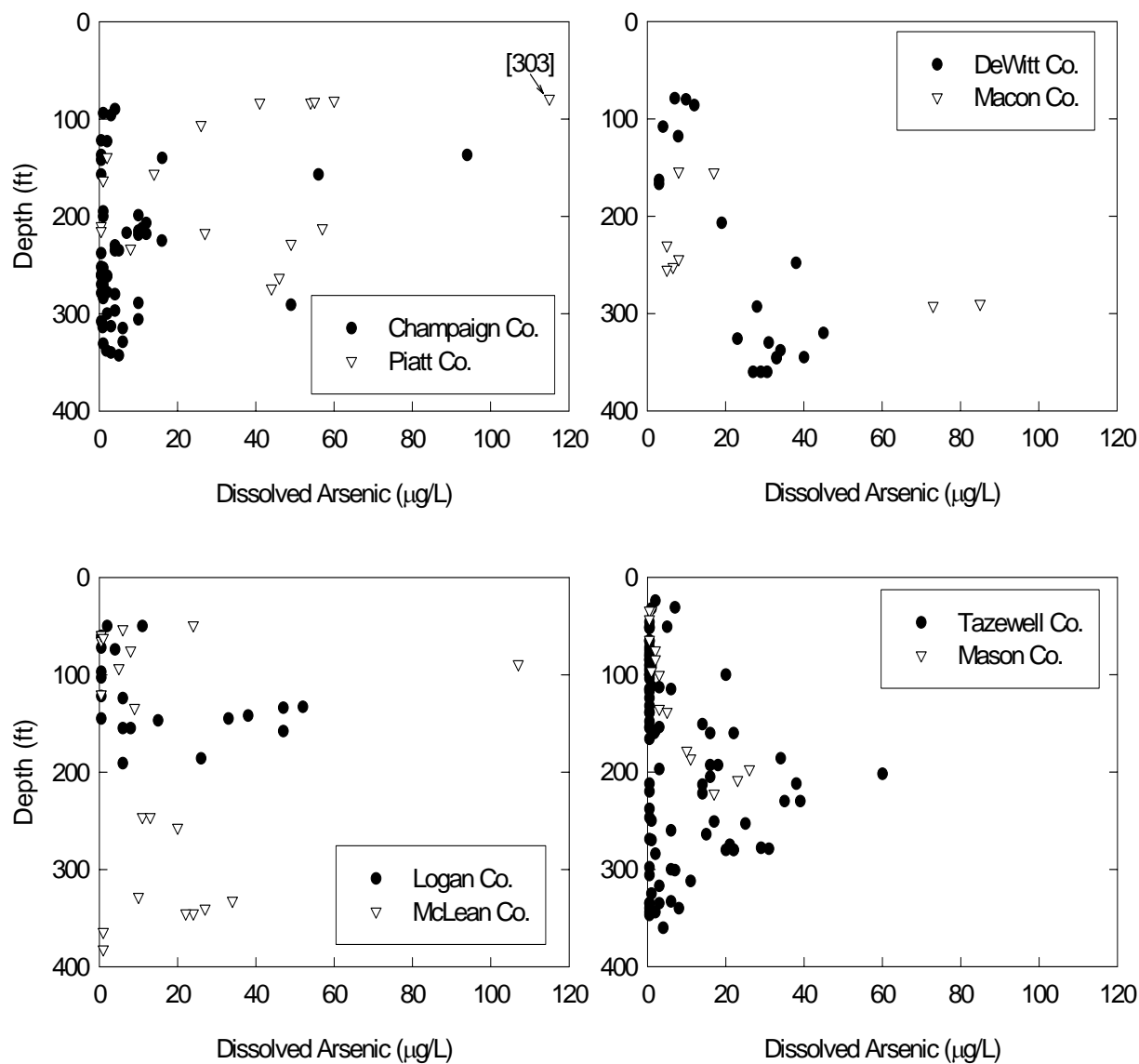
Figure 5. Median arsenic concentrations as a function of well depth for community wells in the Mahomet and overlying aquifers west of and including Champaign County. Data are from the IEPA ambient water quality database, 1980-1999.

Arsenic speciation in the Mahomet Aquifer was done in two studies. For ten samples from private wells, WARNER et al. (2000) determined that the predominant form was As(III). HOLM and CURTISS (1988) determined arsenic species for 18 community wells in the Mahomet Aquifer and 20 private wells in Tazewell County. They found that the number of wells with mostly As(III), mostly As(V), and roughly equal concentrations of As(III) and As(V), were about the same. Most available data from the Mahomet Aquifer, however, are for total arsenic only.

In order for high-arsenic groundwaters to form on a regional scale, two key factors are necessary: (1) a geochemical process to release arsenic from the solid phase; and (2) mechanisms to prevent the arsenic from being transported away (SMEDLEY and KINNIBURGH, 2002).

While there are several important arsenic minerals (e.g., arsenopyrite (FeAsS) and orpiment (As_2S_3)), most arsenic in the solid phase is associated with common iron minerals, specifically iron oxyhydroxides (e.g., FeOOH) and pyrite (FeS_2). Arsenic may be released from these minerals by desorption or due to reductive dissolution of the arsenic-bearing mineral. The most common cause of widespread arsenic contamination is thought to be release from iron oxyhydroxides, probably due to the reaction of iron oxyhydroxides with organic carbon (WELCH et al., 2000). The onset of strongly reducing conditions capable of iron reduction can release arsenic into solution (SMEDLEY and KINNIBURGH, 2002). Oxidation of sulfide minerals such as pyrite is also an important source of arsenic, and has been identified as the primary source in aquifers in Wisconsin and Michigan (SCHREIBER et al., 2000).

Arsenic sorbs to many common aquifer materials, such as metal oxides and clays, and this is what is thought to limit the mobility of arsenic in aquifer systems. For example, hydrous ferric oxide (HFO) sorbs both As(V) and As(III) (PIERCE and MOORE, 1982). If HFO is subsequently reduced, the sorbed arsenic may be re-released into solution. At neutral pH values As(III) is more mobile than As(V) because it is less strongly adsorbed on most mineral surfaces. Aqueous carbonate, ferrous iron, and organic matter (OM) in groundwater can influence the sorption of arsenic. Sorption of carbonate at common groundwater concentrations significantly reduces the sorption capacity of arsenic on HFO, and high concentrations of carbonate could cause the displacement of arsenic (APPELO et al., 2002; KIM et al., 2000). Silica and phosphate may also interfere with arsenic sorption or promote arsenic desorption (HOLM, 2002; MANNING and GOLDBERG, 1996; MENG et al., 2000; SWENDLUND and WEBSTER, 1999). Organic matter may influence arsenic sorption to HFO (REDMAN et al., 2002) and, as a result, increase arsenic mobility in aquifer systems. High concentrations of free sulfide due to sulfate reduction reactions may cause precipitation of sulfide minerals, such as As_2S_3 or FeAsS, removing arsenic from solution (RITTLE et al., 1995; SMEDLEY and KINNIBURGH, 2002).

Treatment of Arsenic-containing Water
Arsenic is inadvertently removed from community water supplies by conventional water treatment processes such as iron removal and lime softening. The efficiency of arsenic removal is highly variable (MCNEILL and EDWARDS, 1995). Table 3 presents arsenic concentrations in untreated and finished water at several water treatment plants that use Mahomet Aquifer water. Arsenic removal efficiency is affected by the pH and concentrations of phosphate, silica, and carbonate/bicarbonate (HOLM, 2002).

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Table 3. Arsenic concentrations in untreated and finished water at water treatment plants pumping water from the Mahomet Aquifer.		
Municipality	*Untreated Water (Fg/L)**	*Finished Water (Fg/L)[†]*
Monticello	53	11
Danvers	47	28
Clinton	36	19
Kenney	38	19
McLean	32	28
Mason City	20	20
Stanford	17	8
Hoopeston	19	5
Armington	16	4
Hopedale	14	12

Notes:
  * NRDC (2000)
  [†] IEPA Water Quality Database

METHODOLOGY

Site Selection

Selection of Community Supplies

As a result of the potential regulatory concerns and added costs to community water supplies resulting from lowering the arsenic MCL, the IEPA compiled a list of community water supplies in Illinois that had source (raw) water arsenic concentrations above 10 Fg/L, and of those facilities that would potentially exceed the new MCL in their finished (treated) water. There were more than 20 supplies on the IEPA list that were utilizing the Mahomet Aquifer. From those 20 supplies, 11 were chosen that represented a cross-section of treatment types and that were geographically spread throughout the Mahomet Aquifer region (Figure 6).

Selection of Study Areas

Because the TCHD data set indicated that Tazewell County has many wells with high arsenic concentrations, it was selected as one of the study areas. In the TCHD study, however, only the arsenic concentrations and well locations were publicly available. There was no information about well depths or from which aquifer the wells were withdrawing water. The fact that the private well data showed such significant amounts of arsenic, even though many of the community wells in Tazewell County had moderate to low arsenic in their supply wells, suggested that elevated arsenic concentrations might be found in shallow parts of the Mahomet Aquifer or in overlying aquifers, where many of the private wells are finished. Champaign County, on the other hand, was selected for the opposite set of circumstances. Little aquifer assessment work has been completed in the eastern portions of the Mahomet Aquifer (Champaign, Ford, and Vermilion Counties), so there were very few private well arsenic analyses to correlate with the geological conditions. Most of the available data were from the IEPA municipal well database. Although most of the community wells in Champaign County were relatively free of arsenic, there were two wells that had arsenic concentrations greater than 50 Fg/L. These data suggested that the levels of arsenic in the Mahomet Aquifer in Champaign County could sometimes be significant.

A study of forty boreholes drilled to bedrock in Tazewell County in a recent ISWS project showed that the Mahomet Aquifer was much more complex than previously suspected (HERZOG et al., 1995; WILSON et al., 1994; WILSON et al., 1998). Because some of the geologic and depositional features of Champaign and Tazewell Counties are similar, it was thought that the same geologic complexity may exist in Champaign County. This, in turn, suggested that some private wells in Champaign County may have elevated arsenic levels as found in Tazewell County.

Selection of Private Wells

One of the goals of the study was to determine whether differences in arsenic concentrations in the Mahomet Aquifer depended on the depth of the well screen within the aquifer, and specifically whether arsenic concentrations tended to be highest in the top, middle, or bottom portions of the aquifer. WARNER (2000) concluded that greater arsenic concentrations were found
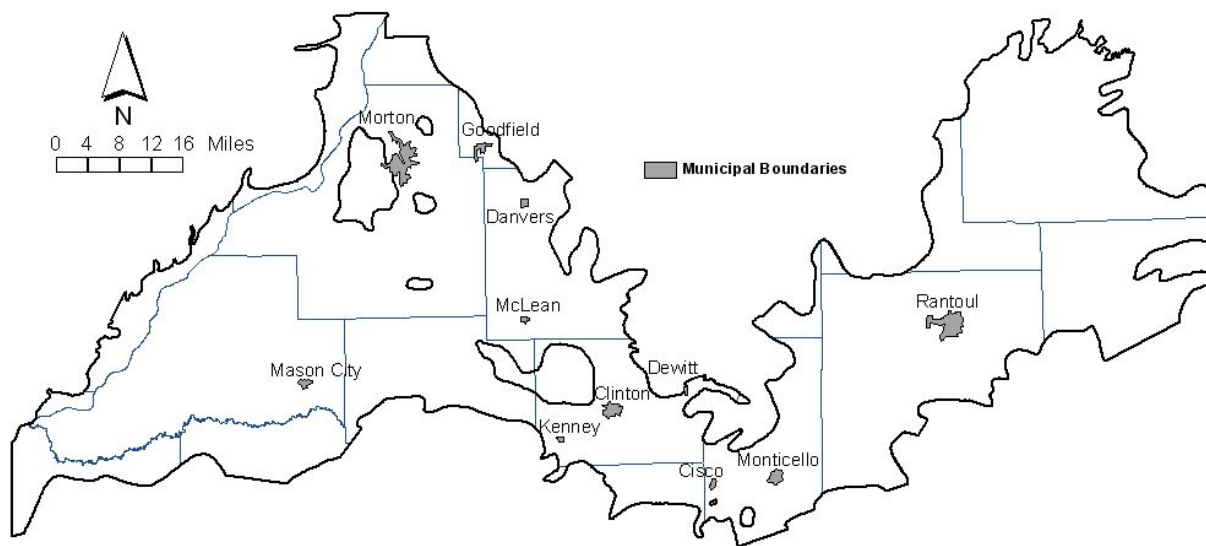
Figure 6. The eleven communities sampled in this study.

in the deep portions of the aquifer, but the TCHD results suggested that samples from the top of the aquifer might have greater concentrations.

The ISWS is developing a regional groundwater flow model of the Mahomet Aquifer. As part of that effort, the regional bedrock surface and aquifer thickness were mapped. Using the bedrock elevation and aquifer thickness, ISWS water well records were evaluated to estimate the elevation of the screened interval for each well and its vertical position within the aquifer. Plotting these data along with the aquifer thickness allowed wells to be selected within specific vertical sections of the aquifer. The aquifer was divided into thirds for the purposes of well selection. Our goal was to sample 50 wells in each county with approximately one-third of the wells in each of the upper, middle, and lower sections of the Mahomet Aquifer. If the confining layer were the source of the arsenic, then one would expect the wells in the upper third to have a higher average concentration of arsenic. Similarly, if the bedrock were the source of the arsenic, then one would expect the wells in the lower third of the aquifer to have higher average arsenic values. To strengthen the comparability of data between different aquifer vertical sections, we attempted to locate groups of wells that were in close geographic proximity and that had wells in all three vertical portions of the aquifer. In addition, several wells were selected that were finished in the shallow Glasford Aquifer, above and separated from the Mahomet Aquifer by a thick clay till.

Champaign County
The procedure for well selection was initially developed using Geographical Information System (GIS) techniques to select the wells based on known well depths and estimates of the top and bottom elevation of the Mahomet Aquifer from previous modeling studies of the Mahomet. We found, however, that for Champaign County, the regional mapping of the aquifer top and bottom was not accurate enough at specific well locations to ensure that the position of the wells within the aquifer could be estimated accurately. In some cases the well logs indicated a thickness that was quite different from the calculated thickness from the regional (model) maps. Therefore, a much more detailed review of each individual log was completed and new interpretations of aquifer thickness at the individual well locations were developed. Wells were then selected based on the updated aquifer thickness information.

We found that there are not as many deep wells in Champaign County as we had assumed; we were only able to find and get permission to sample 12 deep wells. Altogether, 42 wells from the Mahomet Aquifer and 8 Glasford Aquifer wells were selected for sampling.

Tazewell County
The wells selected in Tazewell County mostly came from a set of private wells that the ISWS used in a groundwater resource evaluation in the mid-1990s (WILSON et al., 1998). We already had a relationship with the well owners, had visited the wells in the past, and had a well log for each well. Additional wells to be sampled were selected by searching the ISWS well records and identifying wells that were less than 5 years old and that fit our depth and location criteria.

Sample Collection

Sample Containers and Preservatives
Table 4 lists the sample containers and preservatives used. The containers for arsenic and metals were cleaned by filling with 8% (v/v) HCl, soaking at least 24 hours, and thoroughly rinsing with deionized water.

Special care was taken in collecting and storing groundwater samples for arsenic speciation. There is no consensus in the literature about preserving arsenic speciation in water samples. Although some authors have found that As(III) oxidation was apparently inhibited by acidification (AGGETT and KRIEGMAN, 1987; BORHO and WILDERER, 1997; VOLKE and MERKEL, 1999), others have found the opposite (CABON and CABON, 2000; EATON et al., 1998). For the present work it was decided that acidification was important because Mahomet Aquifer water typically has 0.5-5.0 mg/L Fe^{2+} in solution, and Fe^{2+} oxidation might cause some arsenic to be sorbed. We used HCl as a preservative to avoid any oxidation of As(III) by HNO_3.

The preservative was added to the bottles before leaving on a sampling trip. Addition of preservative was performed in a class-100 clean air bench. Powder-free gloves were worn when handling the bottles. Bottle sets, consisting of one bottle for each analyte in Table 4, were assembled in two-gallon Zip-Lock® bags. Some bags also contained an extra bottle for spiking with a mixture of As(III) and As(V).

Sample Collection from Community Wells
Before each sampling trip a multi-probe instrument for real-time measurement of temperature, specific conductance (SpC), pH, oxidation-reduction potential (ORP) using a platinum electrode, and dissolved oxygen (DO) (Mini-Sonde®, Hydrolab, Austin, TX) was calibrated according to the manufacturer's directions. The treatment plant operators showed the sampling crews the locations of the sampling taps. The Hydrolab® flow cell was connected to the raw water tap and the readings were monitored until the values stabilized. The final readings were recorded along with the date, time, and sampling location. The readings were considered to be stable if the change in one minute was less than: temperature 0.1EC, SpC 5% of the initial value, pH 0.02 unit, ORP 5 mV. The readings typically stabilized within 5-10 minutes except for DO, which continued to drift downward. The DO probe responded very slowly to DO concentrations below ~ 1 mg/L, so if the DO reading fell to less than ~0.8 mg/L and was still falling, it was assumed that the DO was undetectable and the sample was then collected. Because of the high flow rates and the time necessary for the readings to stabilize, it was assumed that the well and piping were completely purged prior to sampling. In fact, many of the wells were operating when the sampling crew arrived at the site.

After the values of temperature, etc. were recorded, the flow cell was disconnected from the sampling line. One member of the sampling crew put on a pair of powder-free gloves. This person was the only one to handle sample bottles. Unfiltered samples were collected for TOC and total arsenic. The sample tube was then connected to a 0.45 µm filter capsule (Gelman) and filtered samples were collected for arsenic species, metals, anions, alkalinity, and ammonia-N. The arsenic species sample was immersed in an ice-water bath immediately after collection.

Table 4. Sample containers, preservatives, and holding times.			
Analyte	*Container Material*	*Preservative[4]*	*Holding Time (days)*
Arsenic Species[1]	HDPE[2]	0.3% HCl	1
Total Arsenic[3]	HDPE	0.2% HNO_3	30
Metals	HDPE	0.2% HNO_3	180
Anions/Alkalinity	HDPE	None	2
Ammonia-N	HDPE	0.2% H_2SO_4	24
Nonpurgeable Organic Carbon	Glass	0.5% H_2SO_4	ASAP[5]

Notes:

[1] 0.45 mm filtered samples.

[2] HDPE high-density polyethylene.

[3] Unfiltered.

[4] Percent by volume of concentrated high-purity acid.

[5] Holding time not specified for acidified samples.

After all of the samples were collected the bottles were returned to their Zip-Lock® bag and the bag was stored in a cooler with ice. After the raw water samples were collected a set of treated water samples was collected by the same procedure.

Sample Collection from Private Wells

Private wells were sampled from outside taps. Unlike the community wells, the private wells could not be assumed to be completely purged by the time the readings stabilized. Furthermore, most systems had a pressure tank upstream from the sampling tap. Therefore, both the well and pressure tank had to be purged to obtain a reliable sample from a private well. A Y-connector was attached to the tap. A garden hose was connected to one branch and the Hydrolab® flow cell was connected to the other one. The tap was turned to the maximum flow and most of the flow went through the hose. The temperature, pH, etc. were monitored as for the community wells. The flow rate was measured with a two-gallon bucket and a stopwatch. Flow rates were typically 3-7 gallons per minute.

For a completely-mixed tank containing a tracer at concentration C_0 and an influent stream with no tracer, the tracer concentration decreases exponentially with time (LERMAN, 1979):

$$C = C_0 e^{-\frac{t}{\tau}}$$ **(1)**

where C is the tracer concentration, t is time, and τ is the residence time (tank volume divided by flow rate). For a typical 20-gallon pressure tank, the residence time for flow rates of 3, 5, and 7 gallons per minute is 6.7, 5.0, and 2.9 minutes. The degree of purging for 2, 3, and 4 residence times is 86%, 95%, and 98%. Each well was purged for 15 minutes, which was determined to be long enough for at least 95% flushing. All measurements (temperature, pH, etc.) except DO always stabilized within 15 minutes. After purging, the readings were recorded and samples were collected using the same procedure as for the community wells.

EDWARDS et al. (1998) suggested that a significant fraction of the arsenic in groundwater may be in particulate form and that some of the particles are small enough to pass through a 0.45 μm filter. We investigated this by using two sizes of filters, 0.45 Ϝm (the usual operational definition of "dissolved" substances) and 0.02 Ϝm, for approximately half of the Tazewell County samples. A peristaltic pump was connected to the outlet of the 0.45 μm filter capsule to provide the pressure needed to force water through the 0.02 μm syringe filters. The 0.02 μm filtrate used the same preservative as the other samples for arsenic determination.

Sampling Quality Assurance
Each sampling crew collected one extra arsenic species sample per day. This sample was spiked with a mixture of As(III) and As(V) to check for species stability. In most cases, this was done at the first sampling site of the day. Each day at least one crew collected a set of blanks by pumping deionized water through the sampling tubing and filter capsule with a peristaltic pump.

Sample Storage
Samples for arsenic speciation, anions/alkalinity, ammonia-N, and nonpurgeable organic carbon were stored at 4EC. Arsenic speciation was determined as soon as possible after sample collection, usually within 24 hours. Recoveries of field spikes were within 80-120%, a typical data quality objective. Therefore, sample preservation and storage appeared to be adequate.

Chemical Analyses

Total Arsenic and Dissolved Arsenic
Arsenic concentrations were determined by inductively coupled plasma mass spectrometry (ICPMS). The arsenic concentrations in unfiltered and filtered samples were operationally defined as the total and dissolved arsenic concentrations, respectively.

Arsenic Speciation
A method previously developed at WMRC used an ion chromatography (IC) column and NaOH as the mobile phase. It produced well-separated and well-formed chromatographic peaks, linear calibration curves for both As(III) and As(V), and sub-ppb detection limits. However, the groundwater in almost all parts of the Mahomet Aquifer is saturated with respect to $CaCO_3$ and has moderately high concentrations of ferrous iron (HOLM, 1995; PANNO et al., 1994; WARNER, 2001). Adding NaOH to such water would cause both $CaCO_3$ and HFO to precipitate, which would remove some arsenic from solution and also plug the high performance liquid chromatography (HPLC) column.

Two different tandem ICPMS methods were developed in this project for the speciation of arsenic in groundwater. The first method, identified as IC-ICPMS, is based upon the interface of ion exchange chromatography to ICPMS. The second method, developed in the last stages of the project, uses a reversed phase C-18 column interfaced to the ICPMS, and is designated as HPLC-ICPMS. Both approaches are represented by the schematic shown in Figure 7. In both methods, arsenic species are separated by high-performance liquid chromatography (HPLC) prior to introduction into the ICPMS that serves as the detector.

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Schematic of HPLC (IC)-ICPMS

Solvent delivery

HPLC Pump(s)

Autosampler

6 port HP Sampling Valve on **PrepLab**

Sample Loop or C18 adsorb column

Peripump(s)

0.45 μm Precolumn Filter

Waste

C-18 or Anion IC column

Splitter/Valve
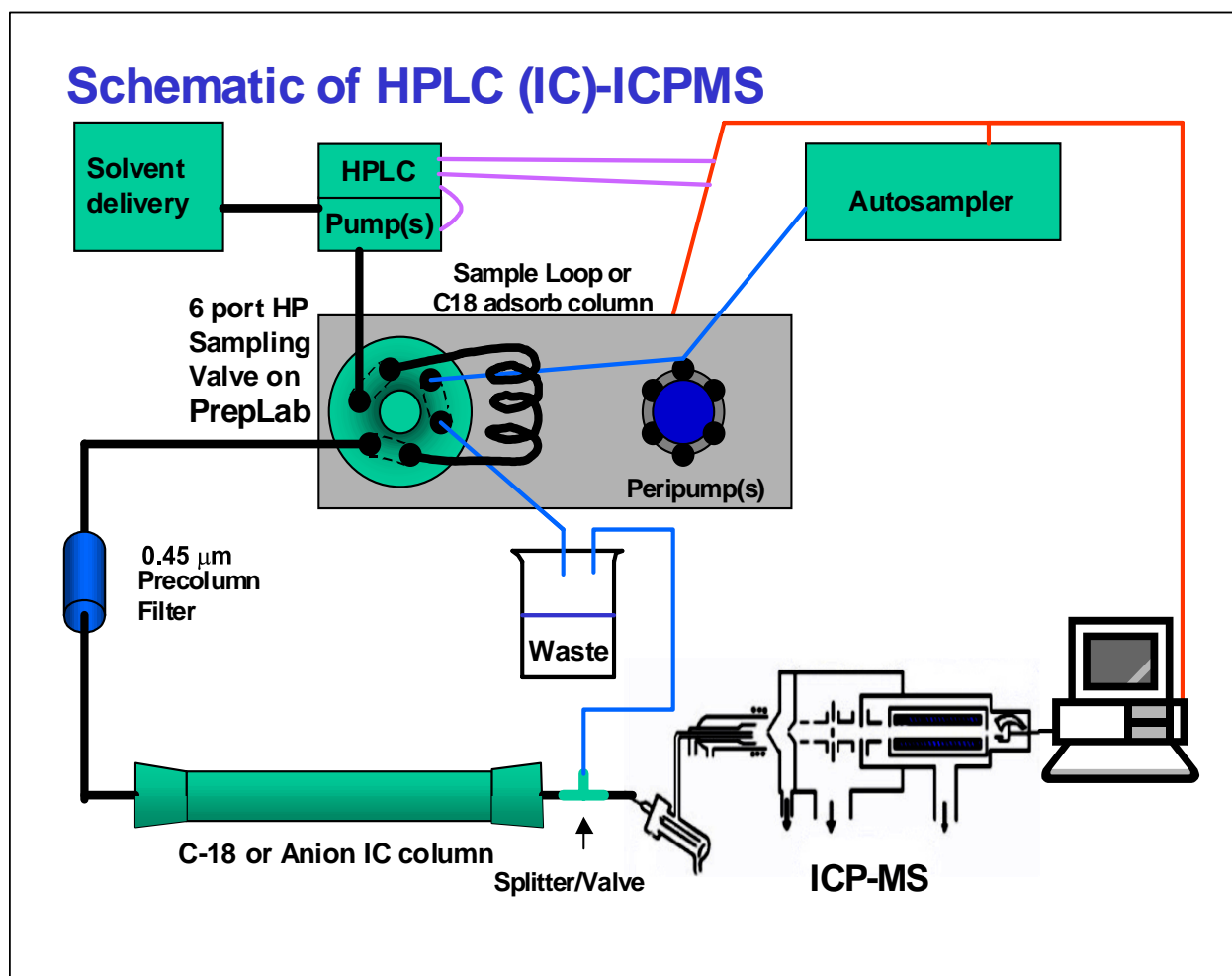
ICP-MS

Figure 7. Schematic of the system used to determine arsenic speciation.

IC-ICPMS Method

Speciation for As(III) and As(V) by IC-ICPMS was achieved by coupling a 4.6x250 mm Dionex AS11 IonPac anion-exchange column to the sample introduction system of the Thermo Elemental PQ ExCell ICP-MS operated in a time domain mode. An HPLC Lab Alliance pump, operated in an isocratic mode, was used to push mobile phase, 2.5 mM phthalic acid at pH ~3, through the column and to the ICP. Automation of the entire IC-ICPMS system was achieved by modifying the sample introduction system of the PQ ExCell with a high-pressure 6 port Valco sampling valve. The sampling loop of the IC system was relatively small (30 µL) so that the sample preservative, 0.3 % HCl, would not exceed the buffering capacity of the eluent and affect retention times of analytes. The column effluent flowed directly into the nebulizer of the ICPMS through 10 µm capillary tubing to minimize peak broadening after the column. Arsenic was measured at m/z 75 on the instrument. Representative IC-ICPMS chromatograms (Figure 8) shows good separation of As(III), As(V), and chloride. Integration over peaks allowed good quantitation of species as demonstrated in the calibration curves illustrated in Figure 9.

Detection limits (3σ, n=7) for these species in groundwater samples were found to be 0.2 ppb and 0.3 ppb for As(III) and As(V), respectively, on 2-fold dilutions of samples. Figure 8 shows that correction for $^{40}Ar^{35}Cl$ interference was not necessary since chloride elutes at a different time than either of the two inorganic species.

HPLC-ICPMS Method

Speciation for arsenite (As(III)), arsenate (As(V)), monomethylarsonic acid (MMAA), and dimethylarsinic acid (DMAA) by HPLC-ICPMS was achieved by coupling a Phenomenex 4.6x150 mm reversed-phase (C-18) Luna column to the sample introduction system of the ExCell ICPMS operated in a time domain mode. In this case, the mobile phase was 2.5 mM phthalate buffer, pH 4.0, and 0.1 % methanol. Octanesulfonate (2 mM) was used as an ion pairing reagent. A larger sample loop still could not be accommodated with this system because the samples were still preserved with 0.3 % HCl. All other instrumental conditions of the IC-ICPMS approach were used here. Chromatograms obtained from the HPLC-ICPMS system are shown in Figure 10 for both a 40 µg/L standard and a groundwater sample spiked with arsenic species at 5 µg/L. As evident from the figure, good separation of all four arsenic species was obtained. For the spiked sample, the HCl preservative caused peak rounding or splitting for DMAA and peak fronting for As(V). However, both peaks were still integrated accurately because the integration windows were set sufficiently large to accommodate slight shifts in peaks. Fronting of the As(V) peak was minimized with the use of a small (30 µL) sample loop. Detection limits for all four species in groundwater preserved in HCl were not formally determined but were easily observed to be < 0.5 µg/L for minimum 2x dilutions of samples, still substantially below the new arsenic MCL of 10 µg/L.

Analysis by IC-ICPMS

Even though groundwater was the only sample type examined in this study, the overall goal for development of an arsenic speciation method is a robust method that is universally applicable to a variety of sample types, not just groundwater. The problem with the IC-ICPMS approach is that
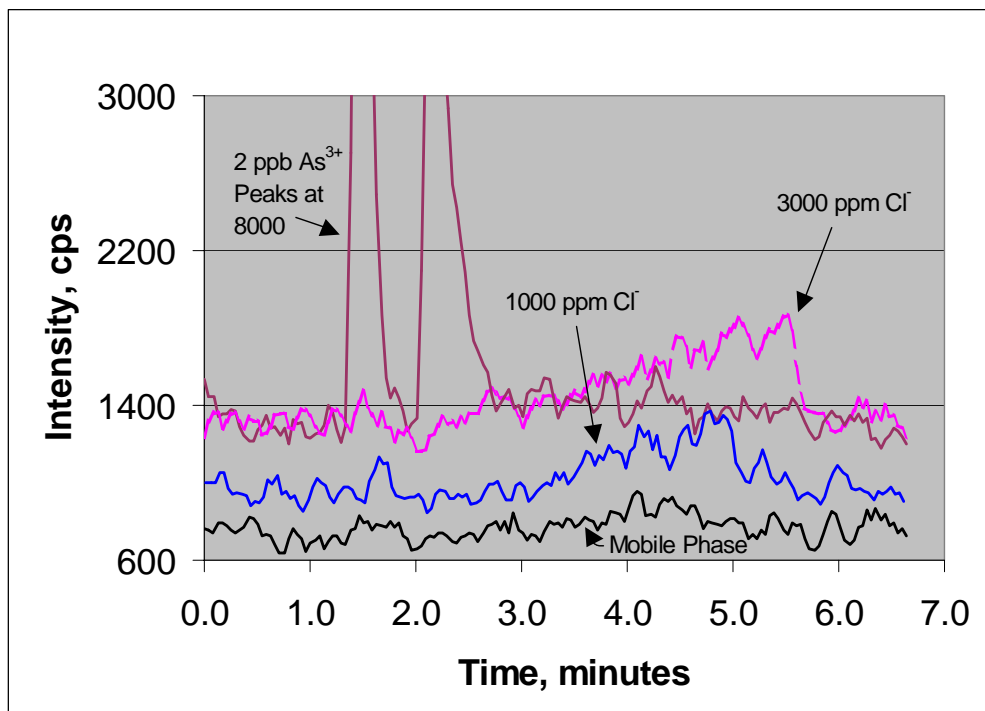
Figure 8. IC-ICPMS chromatograms of the mobile phase, mobile phase spiked with chloride, and mobile phase spiked with As(III) and As(V).
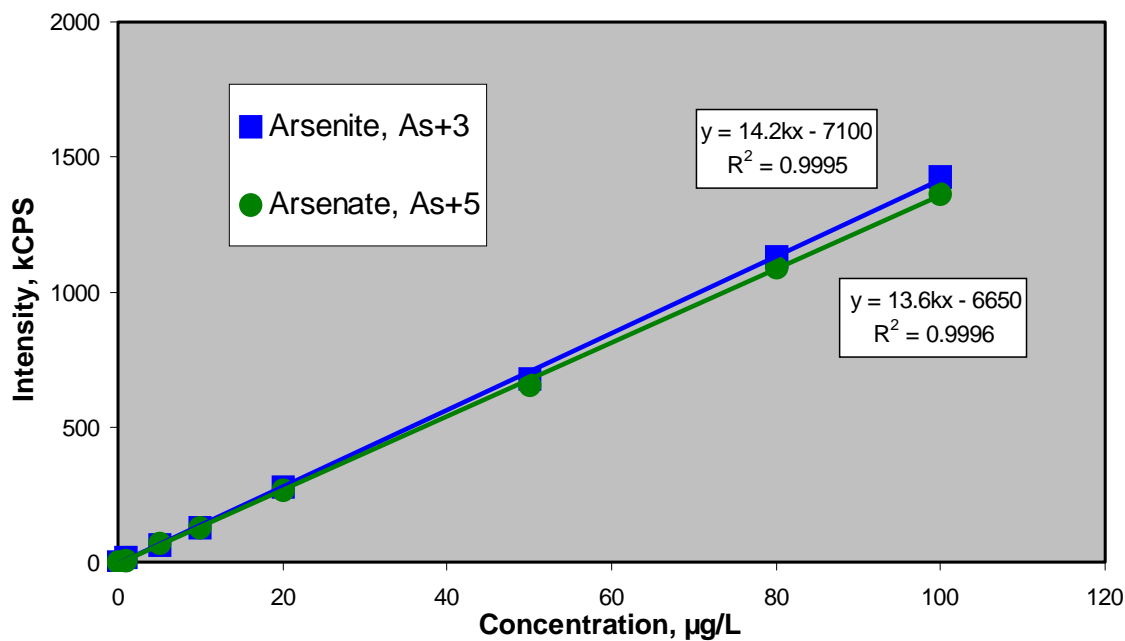
Figure 9. Calibration curves for As(III) and As(V) by IC-ICPMS.
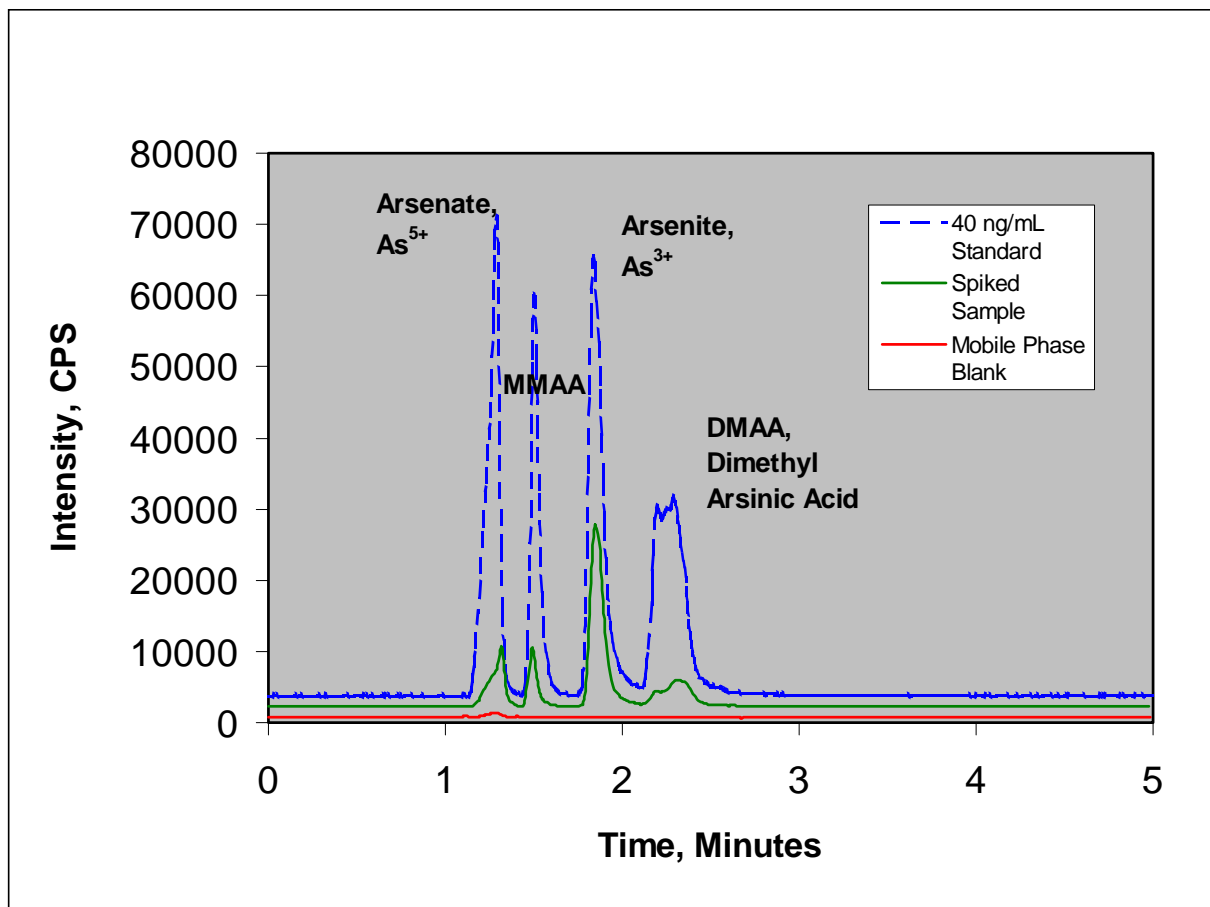
Figure 10. HPLC-ICPMS chromatograms of a standard containing As(V), MMAA, As(III), and DMAA, a groundwater sample spiked with the four arsenic species, and a blank.

the methylated arsenic species, MMAA and DMAA, overlap with As(III) such that the IC-ICPMS method is not able to differentiate between them in surface waters. While MMAA and DMAA are rarely found in groundwater (IRGOLIC, 1982), these species are sometimes found in surface water along with As(III) and As(V) (ANDERSON and BRULAND, 1991; IRGOLIC, 1982). Hence, the HPLC-ICPMS method was developed as it is capable of differentiating and quantifying all four arsenic species.

Precision and Accuracy of the Analysis
Dissolved arsenic was determined by ICP-MS with a correction for the $^{40}Ar^{35}Cl$ interference. The arsenic species were determined by IC/ICP-MS for the municipal and Champaign County samples and by HPLC/ICP-MS for the Tazewell County samples. Both IC and HPLC separated the arsenic species from chloride, so there was no need for a correction. For almost all samples for which both As(III) and As(V) were detectable, the relative difference between the dissolved arsenic concentration and the sum of As(III) and As(V) was less than 10%. The only exceptions were a few samples with less than 1 Fg/L total arsenic. Figure 11 compares dissolved arsenic with As(III)+As(V). There were good correlations for both methods. The slope, intercept, and r^2 value for IC/ICP-MS were 0.97, 0.82, and 0.99, respectively, while for HPLC/ICP-MS they were 0.98, 0.03, and 1.00, respectively. Therefore, there was very little bias for either method. The precision of the speciation analysis was assessed by conducting replicate analyses of the same sample. Seven replicate analyses of sample 102 spiked at just 0.5 Fg/L of both As(III) and As(V) yielded within-run relative standard deviations of 0.5 % and 0.7 %, respectively, for the inorganic arsenic species. These values are well within the data quality objective for precision of analyses for the project.

As the HPLC-ICPMS method was only developed at the very end of this project, no attempt was made to quantify the precision and accuracy of this approach.

Other Analytical Methods
Other analyses besides arsenic were based on standard methods (Table 5). One of the project hypotheses was that arsenic speciation and solubility are consistent with the geochemistry of the aquifer. Therefore a comprehensive analysis was performed for all samples. Another hypothesis was that arsenic is removed at community water treatment plants to varying degrees depending on water chemistry and treatment processes. While this hypothesis is not strictly testable, comprehensive chemical analyses of the raw and finished water at the treatment plants were performed to determine any changes in total arsenic concentrations and arsenic speciation to evaluate which processes and operational variables provide the greatest arsenic-removal efficiency.

Data Analysis and Modeling
Chemical data were compared in a variety of ways. Because most of the data were non-normally distributed, non-parametric tests were used, i.e., rank sum test when comparing two populations and ANOVA on ranks when comparing more than two populations. Dunn's Method was used to determine whether differences between population pairs were significant when results from an ANOVA on ranks test indicated a significant difference. Significance was determined at the 95%
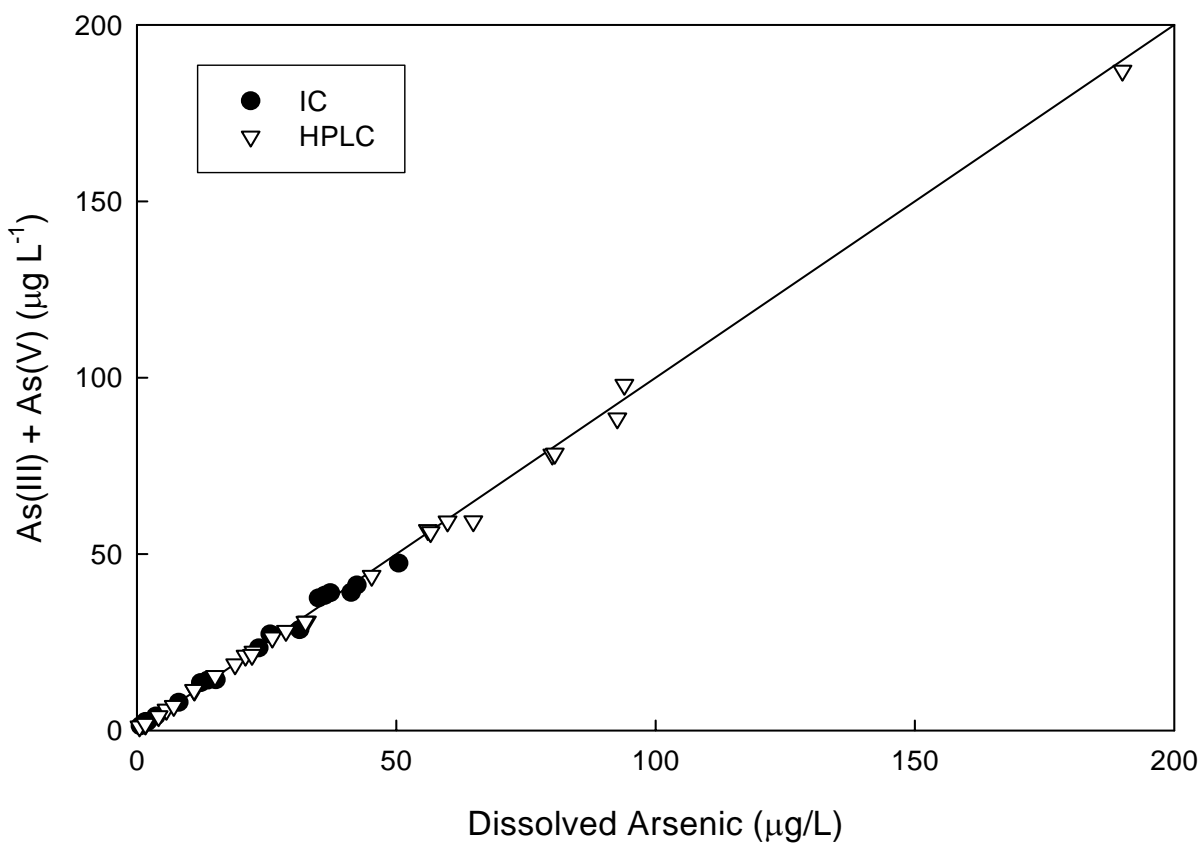
Figure 11. Comparison of sums of arsenic species concentrations determined by IC-ICPMS and HPLC-ICPMS with dissolved arsenic concentrations.

Table 5. Analytical methods besides arsenic speciation.			
Analyte	*Method*	*Reference*	*Laboratory*
NH_3-N	EPA 350.1	USEPA (1993a)	ISWS
Alkalinity	USGS I-1030-85	USGS (1989)	ISWS
Anions (F^-, Cl^-, SO_4^{2-}, NO_3^-, PO_4^{3-})	EPA 300.0	USEPA (1993b)	WMRC
Metals (Ca, Mg, Na, Fe, Mn, P, Si)	EPA 200.8	USEPA (1994)	WMRC
TOC	EPA SW-846/9060	USEPA (1986)	WMRC

level ($P < 0.05$) for all tests. The tests were run using the software package SigmaStat (SPSS, 1997).

The following populations were compared statistically: (1) all data in Tazewell vs. Champaign Counties; (2) all data in each county as a function of vertical location in the aquifer (deep vs. intermediate vs. shallow vs. Glasford); (3) Tazewell County data as a function of SO_4^{2-} concentration; and (4) Tazewell County data as a function of location with respect to the groundwater divide. The rationale for data population selection is discussed more fully in the Results Section.

Chemical equilibrium modeling was done using MINEQL+ (SCHECHER and MCAVOY, 1994) and Geochemist's Workbench© (BETHKE, 2002). Saturation indices were calculated for the water samples for Tazewell County to determine potential solubility controls on Fe, manganese (Mn), and arsenic.

RESULTS

Public Water Supplies

Water samples were collected from municipal water treatment plants in 11 communities in geographically diverse parts of the aquifer. The treatment plants all use water from the Mahomet Aquifer and have a history of arsenic concentrations between 10 and 50 Ｆg/L. For some communities more than one well was sampled. The complete chemical analyses are presented in Table A-3 of Appendix A.

<u>Arsenic</u>

All arsenic concentrations were less than 50 Ｆg/L (Table 6). The total arsenic concentrations in finished water were less than those in unfinished water at all locations. However, the total arsenic concentrations in finished water were below the new MCL of 10 Ｆg/L for only four of the plants, Cisco, Goodfield, Morton, and Rantoul. Although one Rantoul well has had high arsenic concentrations in the past, that well was not in use at the time of sampling. None of the Rantoul samples in the present work had detectable arsenic.

Filtered and unfiltered raw water samples were analyzed to see if a significant fraction of the arsenic was in particulate form. Duplicate samples were collected from four wells to estimate uncertainties due to sampling and analysis. The absolute differences between the arsenic concentrations in unfiltered (total arsenic) and filtered (dissolved arsenic) samples were less than 2 Ｆg/L for all but four wells (Table 7). The unfiltered arsenic concentration was slightly less than the filtered concentration in some samples, which is theoretically impossible. However, the absolute differences between filtered and unfiltered duplicates ranged from 0.5 to 3.1 Ｆg/L. Therefore, for most wells, the differences between filtered and unfiltered arsenic concentrations, positive and negative, were within the overall uncertainty and if there was any particulate arsenic in the raw water there was probably less than ~3 Ｆg/L. There may have been detectable particulate arsenic in Danvers wells 3 and 5. For Danvers well 4, the unfiltered arsenic concentration was 10 Ｆg/L less than the filtered concentration, but the bottles may have been mislabeled.

As(III) was the predominant species in all raw water samples, although As(V) was detected in many samples. The As(III):As(V) ratio ranged from 2 to 18 in the raw waters. As(V) was the predominant form in most finished water samples, which is to be expected because most treatment plants chlorinate to disinfect their water. Chlorination rapidly oxidizes As(III) to As(V) (FRANK and CLIFFORD, 1986).

The correlations between arsenic and the other parameters measured in the community well samples were weak (Figures B-4 and B-5, Appendix B). The best correlations for arsenic were with total organic carbon (TOC) (r^2 0.23) and ammonia-nitrogen (NH_3-N) (r^2 0.22). Because of the variability in arsenic concentrations observed in this and other studies of the Mahomet Aquifer and the large area over which the samples were collected, it is not surprising no strong correlations were observed.

Table 6. Arsenic concentrations in untreated and treated water from water treatment plants.							
Location	*County*	*Well[1]*	*Type*	*As(III)[2]*	*As(V)[2]*	*Dissol. As[2,3]*	*Total As[2,4]*
Cisco	Piatt	3	Raw	26.7	1.87	31.4	30.5
Cisco	Piatt	4	Raw	6.56	< 2[5]	6.95	6.75
Cisco	Piatt	3,4	Finished	< 2	4.74	3.68	NA[6]
Clinton	DeWitt	6	Raw	31.2	< 2	32.3	32.7
Clinton	DeWitt	8	Raw	30.8	< 2	34.7	33.8
Clinton	DeWitt	10	Raw	29.6	< 2	30.7	30.2
Clinton	DeWitt	6,8,10	Finished	< 2	7.60	6.88	20.5
Danvers	McLean	3	Raw	32.8	6.19	37.3	43.0
Danvers	McLean	4	Raw	37.4	3.76	42.4	32.1
Danvers	McLean	5	Raw	32.6	5.63	36.2	41.3
Danvers	McLean	5	Finished	< 2	24.5	25.2	28.1
DeWitt	DeWitt	1	Raw	15.3	< 2	16.9	16.9
DeWitt	DeWitt	1	Finished	< 2	< 2	< 1	18.7
Goodfield	Woodford	1	Raw	16.7	< 2	18.4	17.8
Goodfield	Woodford	1	Finished	< 2	4.10	4.01	4.66
Kenney	DeWitt	1	Raw	35.5	1.99	35.0	35.3
Kenney	DeWitt	1	Finished	< 2	16.3	13.5	15.0
Mason City	Mason	3	Raw	23.5	3.80	25.7	25.7
Mason City	Mason	4	Raw	9.25	4.27	12.3	12.2
Mason City	Mason	5	Raw	14.5	8.86	23.5	22.8
Mason City	Mason	3,4,5	Finished	< 2	21.5	19.3	18.7
McLean	McLean	3	Raw	22.0	< 2	23.6	22.3
McLean	McLean	3	Finished	11.8	2.49	15.2	13.8
Monticello	Piatt	4	Raw	36.6	2.52	41.3	42.2
Monticello	Piatt	4	Finished	< 2	14.9	16.3	16.6
Morton	Tazewell	3	Raw	17.9	< 2	17.8	16.7
Morton	Tazewell	4	Raw	21.4	< 2	19.0	22.1
Morton	Tazewell	6	Raw	18.8	< 2	21.2	19.3
Morton	Tazewell	6	Finished	< 2	< 2	2.21	1.68
Rantoul	Champaign	5	Raw	< 2	< 2	< 1	< 1
Rantoul	Champaign	8	Raw	< 2	< 2	< 1	< 1
Rantoul	Champaign	9	Raw	< 2	< 2	< 1	< 1
Rantoul	Champaign	12	Raw	< 2	< 2	< 1	< 1
Rantoul	Champaign		Finished	< 2	< 2	< 1	< 1

Notes:

[1] Number assigned by community.

[2] Concentrations in $\digamma$g/L.

[3] Dissolved arsenic, 0.45 $\digamma$m filtrate.

[4] Total arsenic, unfiltered.

[5] < 2 or < 1 = below method detection limit.

[6] NA = not analyzed.

Table 7. Arsenic concentrations in filtered and unfiltered raw water samples and absolute differences in arsenic concentrations between duplicate samples (Fg/L).						
		Arsenic Concentrations			*Absolute Differences Between Duplicates*	
Location	*Well*	*Filtered*	*Unfiltered*	*Unfiltered - Filtered*	*Filtered*	*Unfiltered*
Cisco	3	31.4	30.5	-0.9	0.7	0.4
Cisco	4	6.9	6.8	-0.1		
Clinton	6	32.3	32.7	0.4		
Clinton	8	34.7	33.8	-0.9		
Clinton	10	30.7	30.2	-0.5	1.0	2.4
Danvers	3	37.3	43.0	5.7		
Danvers	4	42.4	32.1	-10.3		
Danvers	5	36.2	41.3	5.1	2.0	3.1
DeWitt	1	16.9	16.9	0.0		
Goodfield	1	18.4	17.8	-0.6		
Kenney	1	35.0	35.3	0.3		
Mason City	3	25.7	25.7	0.0		
Mason City	4				0.6	0.5
Mason City	5	23.5	22.8	-0.7		
McLean	3	23.6	22.3	-1.3		
Monticello	4	41.3	42.2	0.9		
Morton	3	17.8	16.7	-1.1		
Morton	4	19.0	22.1	3.1		
Morton	6	21.2	19.3	-1.9		

Geochemistry

The aluminum (Al) concentrations were near or below detection in all samples, which indicates filtration was effective and dust contamination was minimal. For some treatment plants Na concentrations were greater in finished water than raw water and calcium (Ca) and magnesium (Mg) concentrations were lower because of softening. Iron was detected in all raw water samples. At most treatment plants over 90% of the Fe was removed. There was essentially no Fe removal at Mason City, where there was also essentially no arsenic removal. Phosphorus (P) was detected in all raw water samples. Phosphorus concentrations in finished water decreased at all treatment plants except Monticello and Rantoul, where orthophosphate or polyphosphate was added as a corrosion inhibitor, and Mason City, where there was no Fe removal.

The geochemistry of the Mason City wells was distinctly different from the other wells. The Mason City wells had relatively elevated concentrations of Mn and SO_4^{2-} and low concentrations of Fe, bicarbonate (HCO_3^-), NH_3-N, Cl^-, and TOC. These data indicate that conditions are less reducing in this part of the Mahomet. The aquifer is unconfined in Mason County, unlike in most other parts of the aquifer, and the soils are sandy. Therefore, recharge with O_2-saturated

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precipitation is relatively rapid and redox conditions remain relatively oxidizing, keeping Fe and NH_3-N concentrations low.

Except at Mason City, conditions appear to be suboxic (detectable Fe and no detectable O_2 or hydrogen sulfide (H_2S)) for most of the wells. Although we did not analyze for sulfide, there was an unmistakable odor of H_2S for some wells, such as Cisco well 4. The operator at the Goodfield plant said he could sometimes smell H_2S when one of the wells was being pumped, but not the other well. The redox conditions in wells where this occurred were clearly sulfate reducing. Generally, SO_4^{2-} was less than 2.5 mg/L, NH_3-N was greater than 2 mg/L, TOC was greater than 4 mg/L, Fe was greater than 1 mg/L, and Mn was less than 0.05 mg/L for all the wells. Bicarbonate, TOC, and NH_3-N were correlated with one another.

Private Wells
A total of 50 wells were sampled in Champaign County and 48 in Tazewell County. Two samples from Champaign County were discarded because the water had passed through a softener and one sample from Tazewell County was discarded because the water was apparently contaminated by surface runoff down the well bore, as evidenced by near-saturated DO concentrations and very high nitrate (NO_3-N) concentrations. This latter well was noted to be in poor condition and improperly protected at the well head when sampled.

Arsenic
Arsenic was below the method detection limit (MDL) in approximately 40% of the Champaign County samples and 25% of the Tazewell County samples (Figure 12). There was an improvement in the MDL from 0.5 µg/L for the Champaign County sampling event to 0.25 µg/L for Tazewell County. In Champaign County, approximately 90% of the samples had less than 10 µg/L arsenic while the other 10% had between 10 and 50 µg/L. In Tazewell County, approximately 55% of the samples had less than 10 µg/L arsenic, 35% had between 10 and 50 µg/L, and the remaining 10% had between 50 and 200 µg/L.

The wells with arsenic concentrations above 10 µg/L in Champaign County were widely scattered and in some cases were located very near wells with low to undetectable arsenic concentrations (Figure 13).

The wells with high arsenic concentrations in Tazewell County were scattered throughout the study area (Figure 14). As was the case in Champaign County, some of the wells with high arsenic concentrations were located near wells with low or undetectable arsenic. This variability in arsenic concentrations is similar to what was observed in the TCHD data (Figure 2).

Figure 15 summarizes the dissolved arsenic concentrations in the different depth classes. Although the differences in arsenic concentrations among the depth classes were not statistically significant, the samples with the greatest concentrations were from the Glasford Aquifer. The average concentrations for all samples in each class were: Deep 8.1 Ƒg/L (27 samples); Intermediate 10.6 Ƒg/L (31 samples); Shallow 10.6 Ƒg/L (24 samples); and Glasford Aquifer 28.8 Ƒg/L (13 samples). More comparisons are included in Table 8.

30
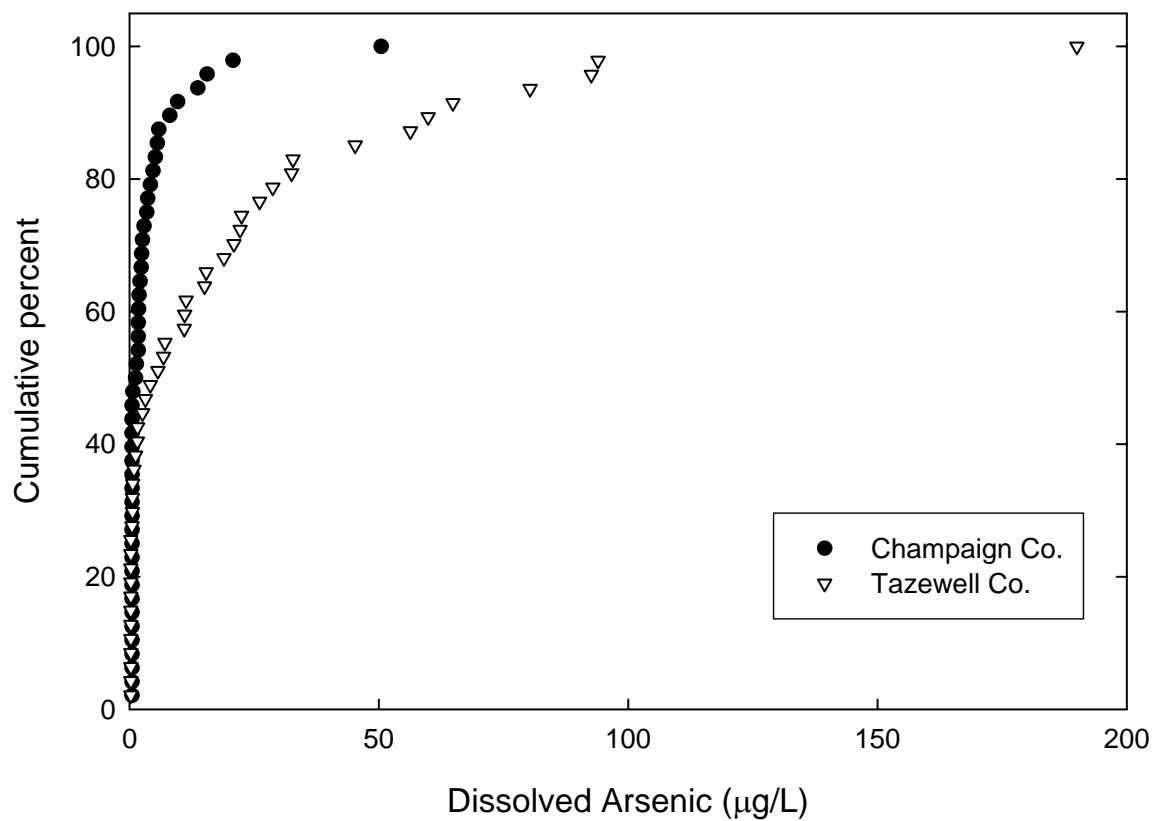
Figure 12. Cumulative distribution of dissolved arsenic concentrations in Champaign and Tazewell County private wells.

31

Arsenic (µg/L)
· < 10
● 10 - 50
● > 50

N

0   2   4   6 Miles
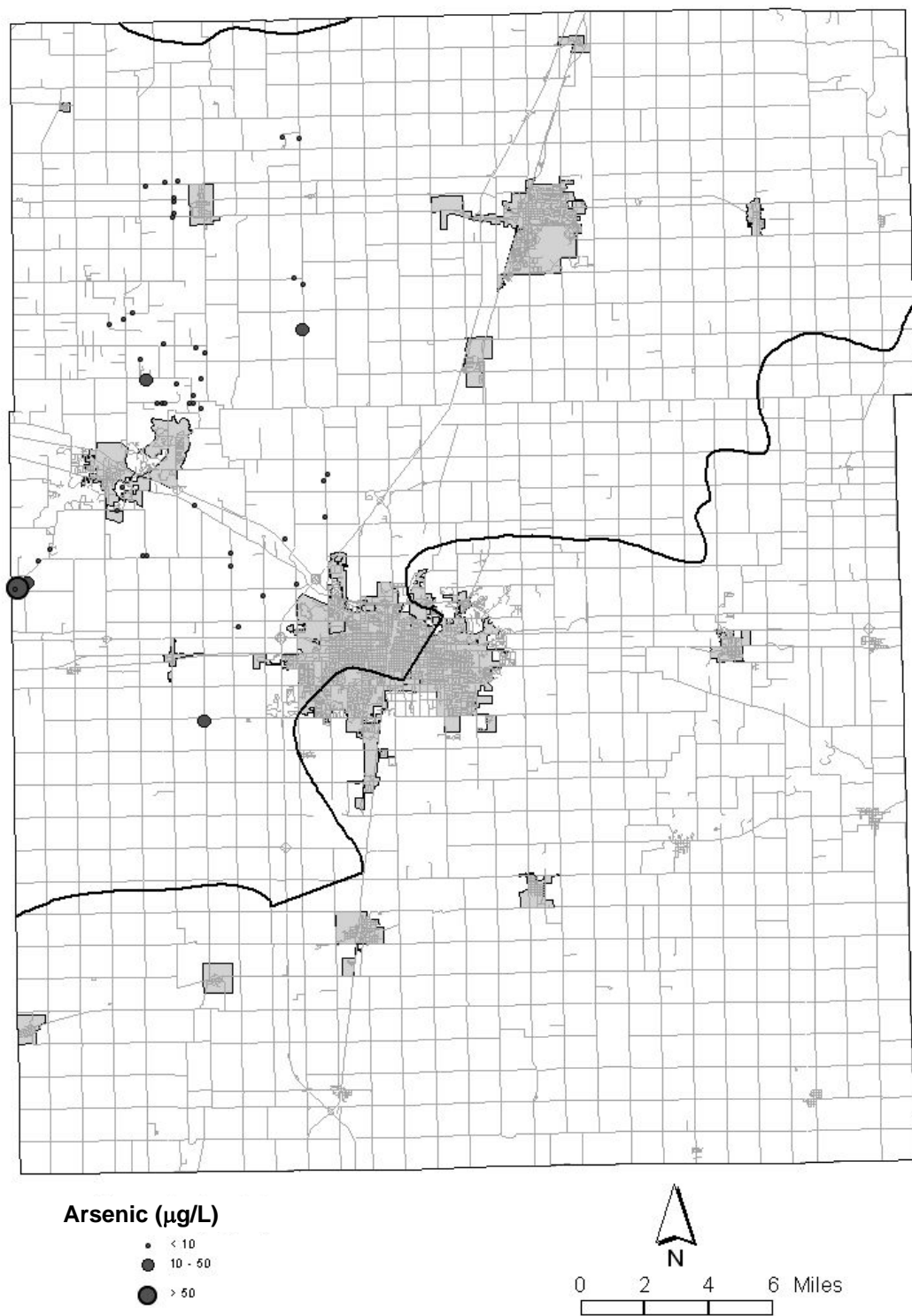
Figure 13. Arsenic concentrations in private wells in northwest Champaign County sampled in this study. The thick solid line bounds the Mahomet Aquifer.

32
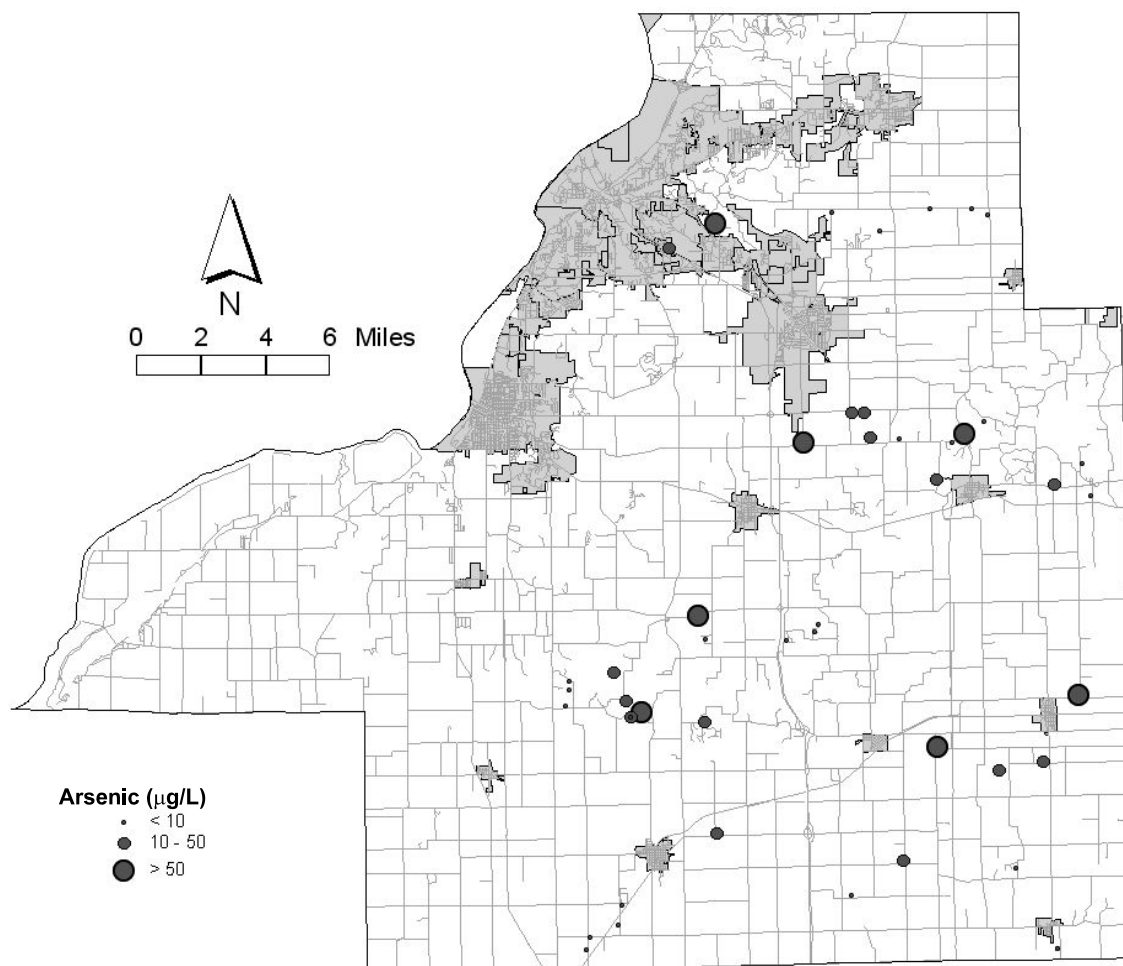
Figure 14. Arsenic concentrations in private wells in Tazewell County sampled in this study.
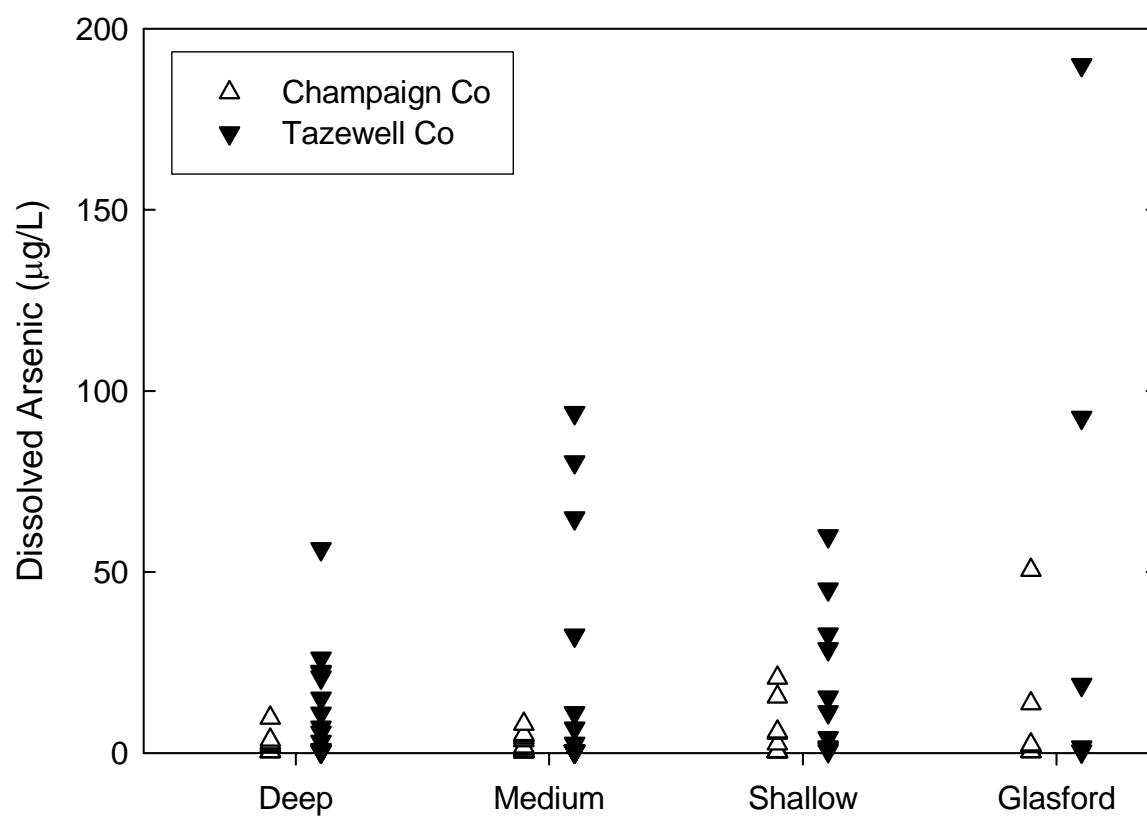
Figure 15. Dissolved arsenic concentrations in the different depth classes.

Table 8. Comparison of arsenic results by county and depth.							
	Number of Samples					*Arsenic (Fg/L)*	
	Total	*Nondetects (%)*	*>10 Fg/L (%)*	*>30 Fg/L (%)*	*>50 Fg/L (%)*	*Maximum*	*Average*
Champaign Co.	**48**	**21 (44)**	**4 (8)**	**1 (2)**	**1 (2)**	**50.0**	**3.8**
Deep	11	3 (27)	0	0	0	9.7	2.3
Intermediate	16	7 (44)	0	0	0	8.0	2.0
Shallow	13	8 (62)	2 (15)	0	0	20.0	4.0
Glasford	8	3 (38)	2 (25)	1 (12.5)	1 (13)	50.0	8.9
Tazewell Co.	**47**	**12 (26)**	**21 (45)**	**10 (21.3)**	**7 (15)**	**190**	**21.1**
Deep	16	4 (25)	7 (44)	1 (6)	1 (6)	56.1	12.0
Intermediate	15	6 (40)	5 (33)	4 (27)	3 (20)	94.0	19.7
Shallow	11	1 (9)	6 (55)	3 (27)	1 (9)	59.9	18.3
Glasford	5	1 (20)	3 (60)	2 (40)	2 (40)	190	60.7
All Samples	**95**	**33 (35)**	**25 (26)**	**11 (12)**	**8 (8)**	**190**	**12.4**
Deep	27	7 (26)	7 (26)	1 (4)	1 (4)	56.6	8.1
Intermediate	31	13 (42)	5 (16)	4 (13)	3 (10)	94.0	10.6
Shallow	24	9 (38)	8 (33)	4 (17)	1 (4)	59.9	10.6
Glasford	13	4 (31)	4 (31)	3 (23)	3 (23)	190	28.8

The Tazewell County wells were divided into 15 groups with at least two depth classes based on geographic location (Figure 16). Ten of these groups had a well in the shallow part of the Mahomet Aquifer. For groups 3, 5, 7, 9, 11, 12, and 14 at least one arsenic concentration was greater than 10 μg/L (Figure 17). For groups 3, 9, and 14 the highest arsenic concentration was in the intermediate Mahomet well. Groups 3 and 14 had their second-highest concentration in the shallow Mahomet well. Group 9 did not have a shallow Mahomet well. Five of the groups included Glasford wells and in two of these (5 and 7) the arsenic concentration was substantially greater than in the Mahomet wells.

As(III) was the predominant species in most groundwater samples. Figure 18 shows the As(V):As(III) ratios for the samples from Champaign and Tazewell Counties as a box and whisker plot. The line in the middle of each box indicates the median value, the ends of the box indicate the 25th and 75th percentiles, the whiskers indicate the 10th and 90th percentiles, and the points outside the whiskers are the extreme values. For example, the median As(V):As(III) ratio for the Champaign County samples with less than 10 Fg/L dissolved arsenic was 0.2. In other words, half of these samples had As(V):As(III) ratios of 0.2 or less. Only one of these samples had more As(V) than As(III). In almost all of the samples from both Champaign and Tazewell Counties with more than 10 Fg/L dissolved arsenic, the As(V):As(III) ratio was less than 0.1.

35
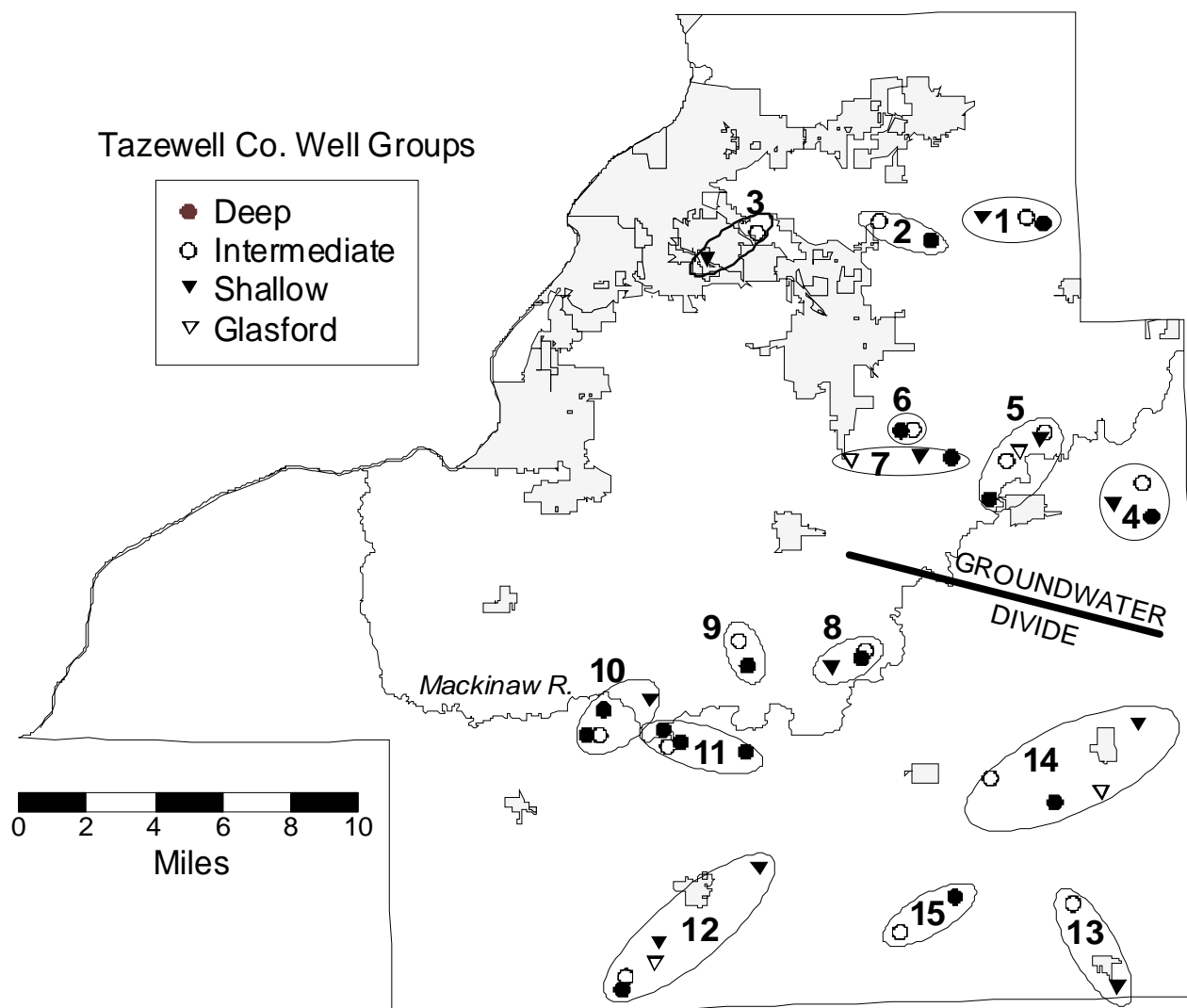
Figure 16. Private wells sampled in Tazewell County, identified by depth class (symbols) and well group (numbers). Filled circle deep Mahomet, open circle intermediate Mahomet, filled triangle shallow Mahomet, open triangle Glasford. Approximate location of groundwater divide shown by straight line.
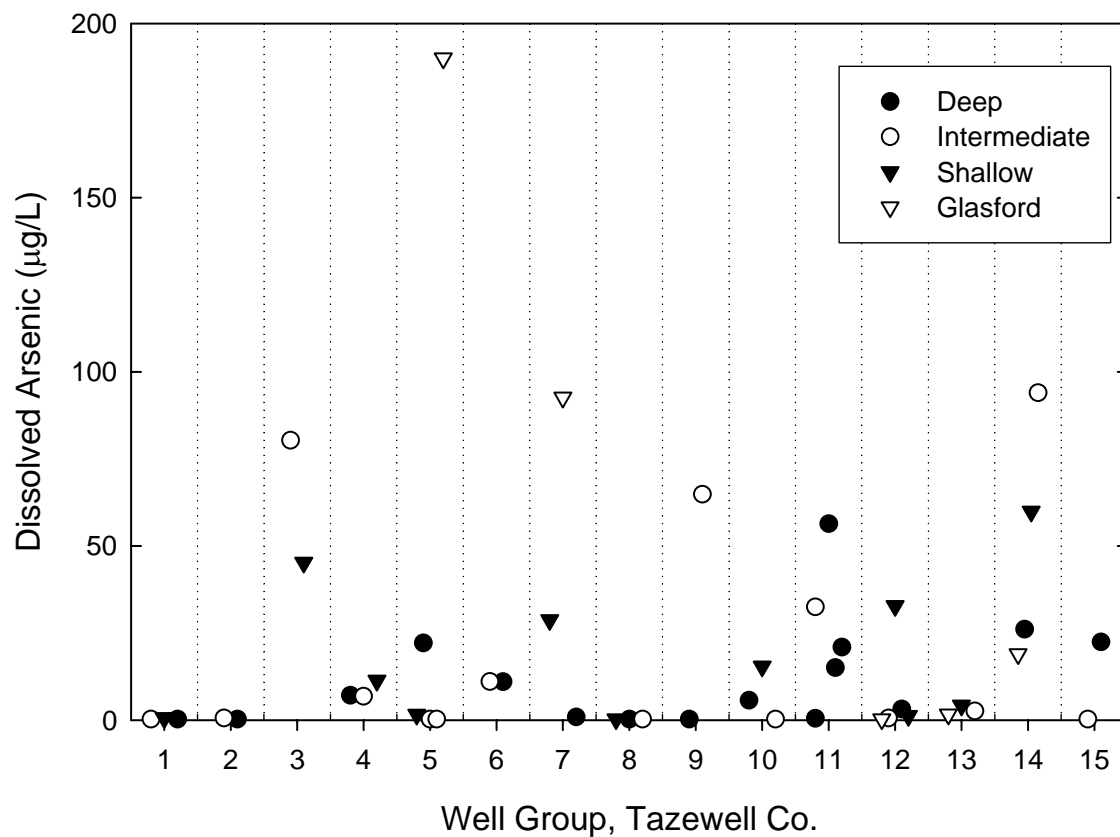
Figure 17. Comparison of dissolved arsenic concentrations in Tazewell County groundwater samples from different well groups and depth classes (see Figure 16).

37
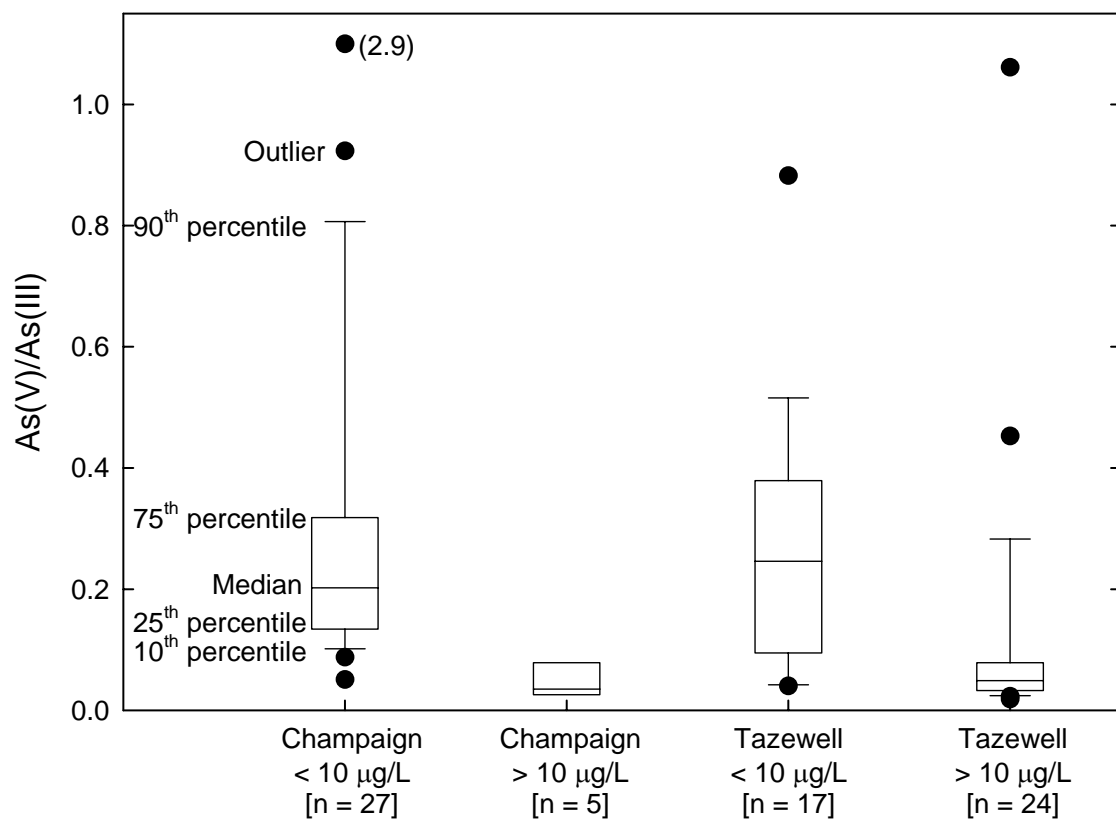
Figure 18. Box and whisker plot of As(V):As(III) ratios in private well samples. The number of samples in each group is designated by n.

For total arsenic concentrations greater than about 10 μg/L, the sum of the As(III) and As(V) concentrations agreed with the total arsenic concentration within 5%. However, for 2-10 μg/L the relative difference was up to 10% and for 1-2 μg/L it was up to 100% (Figure 19).

There appeared to be some particulate/colloidal arsenic in the Tazewell County samples. The difference between the unfiltered and 0.45 μm-filtered arsenic concentrations normalized to the unfiltered concentrations was positive for all samples (Figure 20). However, the difference between the 0.45 μm-filtered and 0.02 μm-filtered samples was negative for about half of the samples, probably because of analytical imprecision. The 0.02 μm-filtered samples were analyzed by graphite furnace atomic absorption. In retrospect, it would have been better to have analyzed these samples by ICP-MS. However, it appears that less than 10% of the arsenic was colloidal.

Groundwater Geochemistry
Dissolved oxygen was less than 1.0 mg/L in all samples in both Champaign and Tazewell Counties. Dissolved Fe was abundant throughout both the Mahomet and Glasford Aquifers, usually greater than 1.0 mg/L, frequently greater than 3.0 mg/L. Manganese was detectable in all samples. Ammonia-N was also abundant throughout the aquifers, typically greater than 2.0 mg/L. One of the Glasford samples had 7.3 mg/L NH_3-N and another had 14.6 mg/L. On the other hand, NO_3-N was very low in most samples. More than half the samples in Tazewell County and one third of the samples in Champaign County had SO_4^{2-} concentrations below the detection limit (0.25 mg/L). The samples were not analyzed for sulfide, but none of the acidified samples had an H_2S odor.

Aluminum concentrations tend to be very low in groundwater due to solubility limitations. When it is detected in groundwater samples, it is usually due to dust contamination during sample collection. All Al concentrations in this study were near the MDL of 1 Ϝg/L, thus dust contamination was improbable. Phosphorus was below the ICP-MS MDL of 0.04 mg/L in over half of the Tazewell County samples but was above the MDL in all but 5 of the Champaign County samples. The silica (Si) concentrations ranged from 5 to 12 mg/L in both counties.

The median TOC concentration was 2.2 mg/L in Champaign County and 2.0 mg/L in Tazewell County. About 23% of the Tazewell County samples had TOC greater than 5.0 mg/L, and about 32% were < 1.0 mg/L. The highest concentrations tended to be in the northern half of the study area. None of the Champaign County samples had TOC greater than 5.0 mg/L.

Figure 21 summarizes the major-ion composition of the Champaign County water samples. Figure 21, a Piper diagram (HEM, 1970), consists of three graphs. The lower-left graph is a ternary diagram that shows the relative concentrations of the cations Ca^{2+}, Mg^{2+}, and $Na^+ + K^+$ expressed as a percentage of the total cation charge (in meq/L). The relative concentrations of Ca^{2+}, Mg^{2+}, and $Na^+ + K^+$ are read by the lines parallel to the Na+K axis, the horizontal lines, and
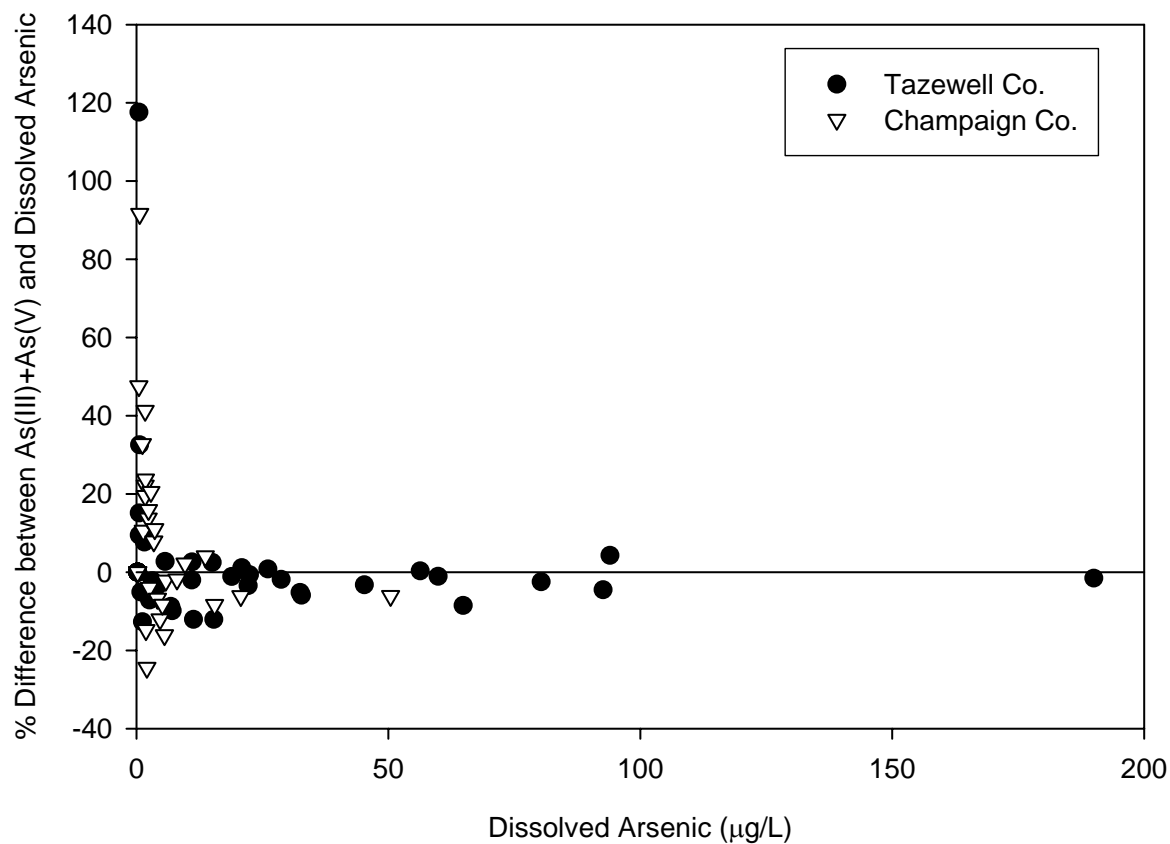
Figure 19. Relative difference between the sum of the As(III) and As(V) concentrations determined by HPLC/ICP-MS and the dissolved arsenic concentration determined by ICP-MS. For each sample, the difference was normalized to the dissolved arsenic concentration.
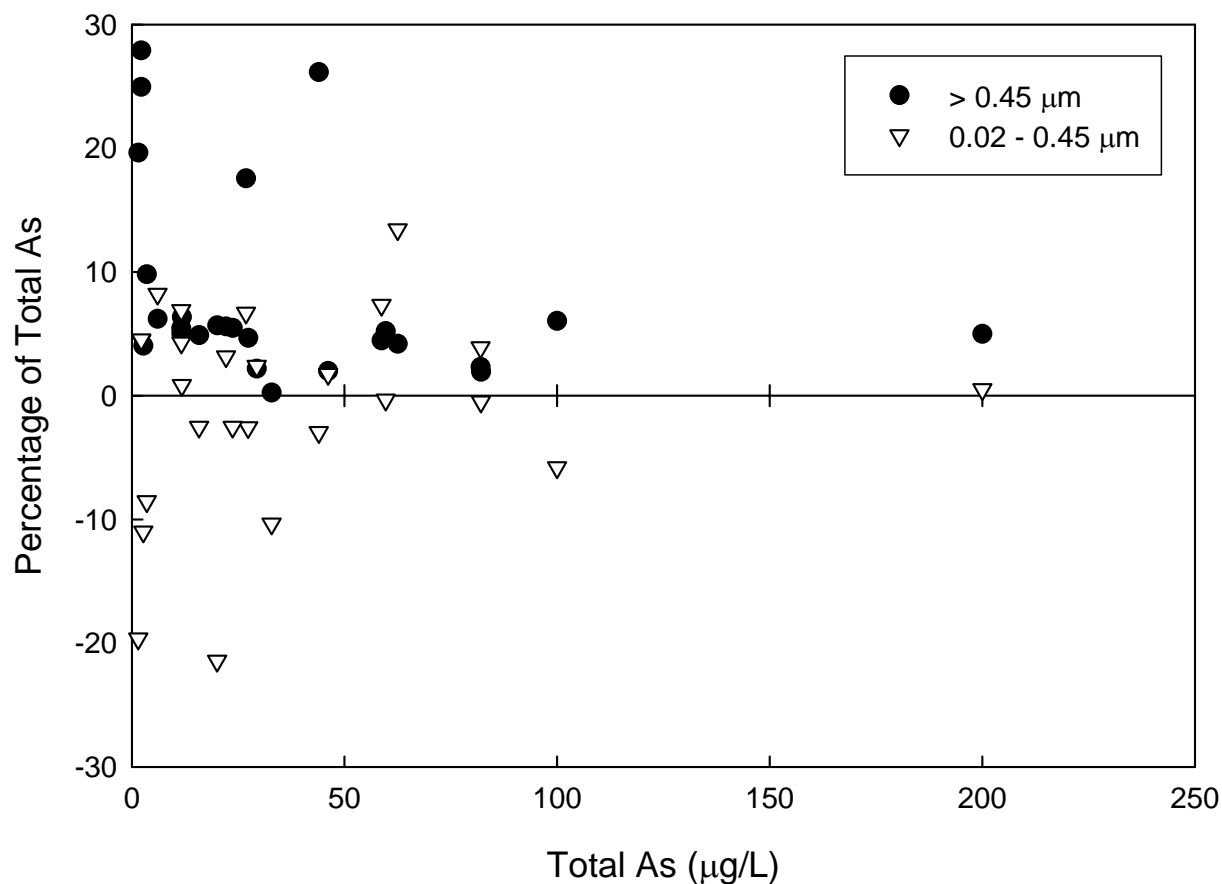
Figure 20. Particulate and colloidal arsenic in Tazewell County samples. Particulate arsenic is the difference between the concentrations in unfiltered and 0.45 μm-filtered samples. "Colloidal arsenic" is operationally defined here as the difference between the concentrations in 0.45 μm-filtered and 0.02 μm-filtered samples. The differences are shown as percentages of the unfiltered concentrations.
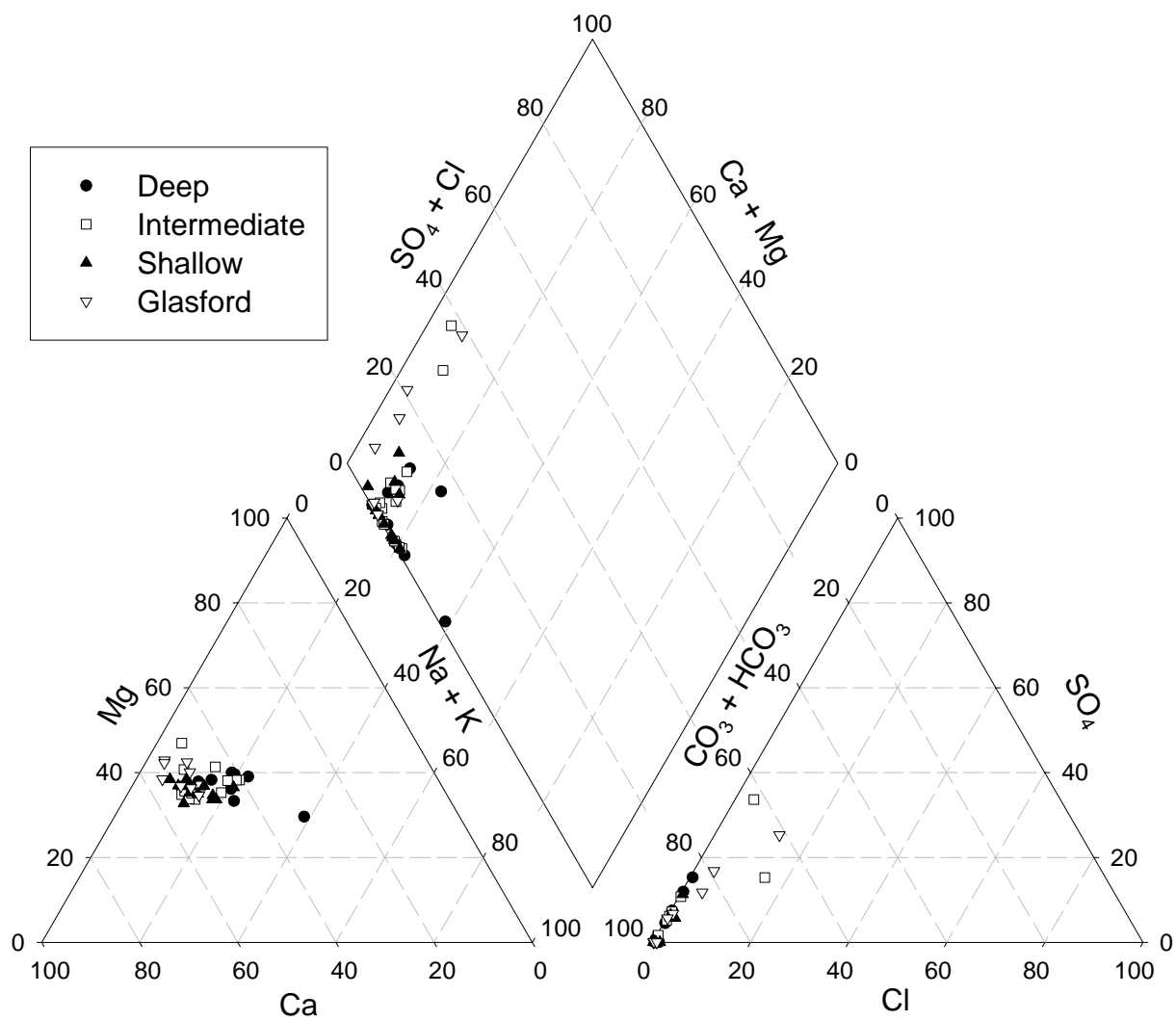
Figure 21. Relative concentrations of major ions in Champaign County private wells. Data separated by depth class.

the lines parallel to the Mg^{2+} axis, respectively. For example, for the point that is separated from the others, Na^+ accounts for approximately 40% of the cation charge while Ca^{2+} and Mg^{2+} account for about 30% each. The anions Cl^-, SO_4^{2-}, and $HCO_3^- + CO_3^{2-}$ are shown in the ternary diagram in the lower-right. The overall composition is summarized in the diamond-shaped graph whose vertices are the intersection of lines through the cation points and parallel to the Mg^{2+} axis and lines through the anion points and parallel to the SO_4^{2-} axis.

In most Champaign County samples Ca^{2+} and Mg^{2+} were the dominant cations. Sodium made up 5-25% of the cation charge, although in one sample Na^+ made up approximately 40% of the charge. Bicarbonate was the dominant anion. Chloride made up 5% or less of the anion charge in all samples but two. There were no apparent differences in major-ion chemistry between the three depth classes of the Mahomet Aquifer and the Glasford Aquifer.

The major-ion chemistry of Tazewell County was similar to that of Champaign County (Figure 22). As in Champaign County, Mg^{2+} accounted for 35-50% of the cation charge. Tazewell County had more samples for which Na^+ accounted for 20-40% of the charge and Ca^{2+} accounted for 30-45% of the charge than Champaign County.

Comparisons between Champaign and Tazewell Counties
There were significantly different concentrations for only a few parameters between the two counties; arsenic, Mg, Mn, fluoride (F^-), and Cl^- were significantly greater in Tazewell than Champaign County (Table 9). Although the SO_4^{2-} concentrations were not significantly different, Tazewell County had many more samples with undetectable SO_4^{2-} than Champaign County. There was also not a great deal of difference in chemistry as a function of aquifer depth class (deep, intermediate, shallow, or Glasford) in either county. In Champaign County, Na was significantly greater in the deep part of the aquifer compared to the Glasford, Fe was significantly greater in the Glasford compared to the deep aquifer, and HCO_3^- was significantly greater in the shallow vs. the intermediate part of the aquifer (Table 10). There were no significant differences among aquifer depth classes for Tazewell County (Table 11).

Comparing the two counties as a function of aquifer depth class, there were several significant differences in chemistry (Table 12). In the deep part of the aquifer, concentrations of Mn and Cl^- were greater in Tazewell County than in Champaign County. Chloride and Mg concentrations were significantly greater in Tazewell County at intermediate and shallow depths. Arsenic (and As(III)) was significantly greater in Tazewell County at shallow depths. There were no significant differences in the Glasford aquifer in the two counties, but relatively few samples were collected therein, and standard deviations tended to be large. As(III) was the dominant form of arsenic in both counties, and this was statistically significant.

Chemical Correlations for Tazewell County
Arsenic did not correlate particularly well with any other constituent (Figures 23 and 24; see also Figure B-1 in Appendix B). There was a positive correlation with NH_3-N, but this relationship may be driven be a single outlier. Elevated arsenic did seem to be associated with relatively high HCO_3^-, TOC, and F^- concentrations, and with low concentrations of Mn and SO_4^{2-}. Other associations that were observed (Figures 25 and 26):
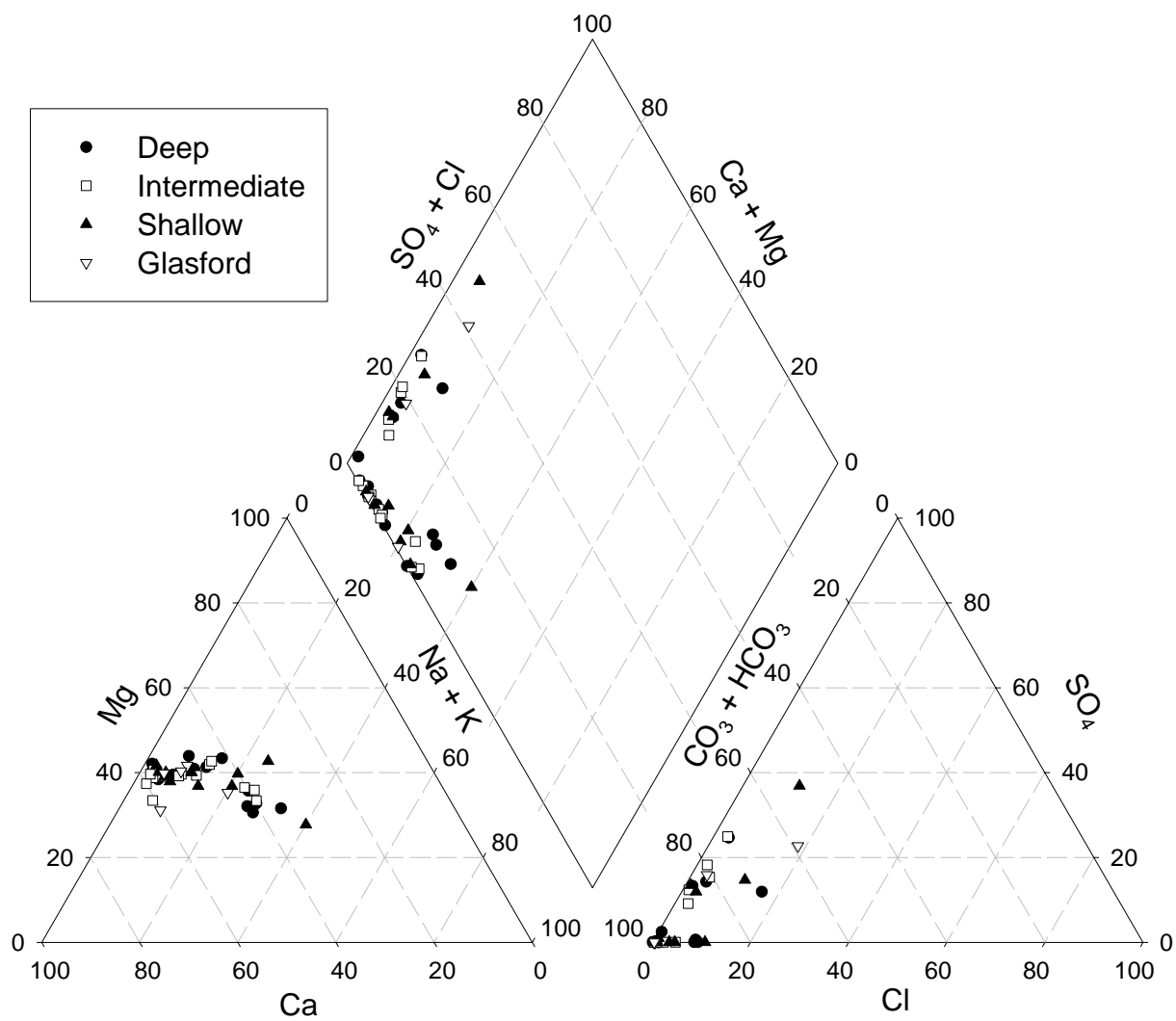
Figure 22. Relative concentrations of major ions in Tazewell County private wells. Data separated by depth class.

Table 9. Comparison of all test results by county using the rank sum test. n = 48 for Champaign County and 47 for Tazewell County. Results in mg/L unless otherwise noted. P values in bold indicate a significant difference (< 0.05).							
	Tazewell Co.			Champaign Co.			
Parameter	Median	25%	75%	Median	25%	75%	P
well depth (ft)	196	144	261	224	199	268	0.126
Dissol. As (Ƒg/L)	4.95	<0.5	24.3	1.30	<0.5	3.55	**0.006**
As(III)	4.28	<0.5	20.9	1.40	<0.5	3.60	**0.006**
As(V)	<0.5	<0.5	1.20	<0.5	<0.5	<0.5	**0.003**
Na	17.7	7.10	36.8	22.4	16.9	29.3	0.162
Mg	36.5	33.8	41.4	32.8	30.7	35.1	**<0.001**
Ca	75.1	70.0	85.5	75.0	60.5	80.0	0.185
Fe	2.01	1.35	3.24	2.07	1.62	2.53	0.950
Mn	0.050	0.022	0.110	0.032	0.022	0.041	**0.009**
Si	8.34	7.70	10.0	9.30	7.60	9.78	0.789
NH_3-N	1.34	0.15	2.96	1.22	0.90	1.60	0.968
TOC	2.11	0.70	4.65	2.00	1.70	2.43	0.991
HCO_3^-	455	387	526	446	421	460	0.332
F^-	0.33	0.28	0.39	0.27	<0.25	0.36	**0.007**
Cl^-	3.75	2.05	11.8	1.10	0.80	1.85	**<0.001**
SO_4^{2-}	<0.25	<0.25	43.4	0.795	<0.25	24.5	0.405
pH	7.22	7.07	7.34	7.10	6.88	7.42	0.364
ORP (mV)	66	52	100	79	53	107	0.427
Conductivity (ƑS/cm)	701	632	805	703	665	801	0.541

	Table 10. ANOVA on ranks results for Champaign County data based on aquifer depth region. Results in mg/L unless otherwise stated. P values in bold indicate a significant difference (< 0.05).												
	Deep; n=11			*Intermediate; n=16*			*Shallow; n=13*			*Glasford; n=8*			
	Median	*25%*	*75%*	*Median*	*25%*	*75%*	*Median*	*25%*	*75%*	*Median*	*25%*	*75%*	*P*
Dissol. As (μg/L)	1.80	<1	2.78	0.95	<1	3.85	<1	<1	5.65	1.95	<1	8.00	0.885
Na	28.0	18.9	35.8	21.9	15.7	26.2	22.6	18.5	30.4	14.5	8.86	20.4	**0.026**
Mg	33.6	25.2	35.1	31.1	27.6	33.9	32.1	31.0	34.3	36.8	32.5	39.5	0.130
Ca	65.2	47.4	77.0	68.9	53.9	79.2	75.6	73.7	81.9	80.1	76.1	88.5	**0.044**
Fe	1.61	1.33	2.18	2.22	1.63	2.70	1.84	1.64	2.51	2.45	2.14	3.09	**0.040**
Mn	0.025	0.019	0.036	0.031	0.021	0.043	0.029	0.021	0.039	0.045	0.034	0.074	0.063
Si	8.00	6.80	9.31	9.07	7.51	9.59	9.46	8.93	10.5	9.53	7.95	9.88	0.097
NH_3-N	1.28	1.10	1.50	1.23	0.94	1.48	1.15	1.03	1.69	0.75	0.13	1.67	0.553
TOC	2.00	1.73	2.35	1.85	1.70	2.20	2.40	1.98	2.95	1.50	1.15	2.30	0.052
HCO_3^-	453	417	455	428	417	452	463	432	468	447	430	460	**0.036**
F^-	0.310	0.158	0.378	0.270	<0.25	0.325	0.260	<0.25	0.333	0.195	<0.25	0.323	0.613
Cl^-	1.10	0.86	1.78	1.02	0.885	1.55	1.30	0.740	1.55	2.50	0.693	13.0	0.800
SO_4^{2-}	0.27	<0.25	26	5.4	<0.25	25.5	0.4	<0.25	5.805	22.75	0.26	62	0.342
As(III)	1.60	<1	3.25	1.10	<1	3.80	<1	<1	4.95	1.90	<1	7.70	0.903
As(V)	<1	<1	0.513	<1	<1	<1	<1	<1	<1	<1	<1	0.825	0.222

Significant differences (P < 0.05) based on Dunn's Method:
Na: Deep > Glasford.
Ca: none.
Fe: Glasford > Deep.
HCO_3^-: Shallow > Intermediate.

	Deep; n=16			Intermediate; n=15			Shallow; n=11			Glasford; n=5			
Table 11. ANOVA on ranks results for Tazewell County data based on aquifer depth region. Results in mg/L unless otherwise stated.													
	Median	*25%*	*75%*	*Median*	*25%*	*75%*	*Median*	*25%*	*75%*	*Median*	*25%*	*75%*	*P*
Dissol. As (μg/L)	6.41	<0.5	21.6	0.590	<0.5	27.1	11.4	1.32	31.8	18.9	1.29	117	0.459
Na	17.7	6.85	53.0	14.2	5.55	24.5	19.5	10.3	38.0	18.5	11.5	30.7	0.751
Mg	35.5	32.9	41.4	35.5	34.6	39.4	37.5	34.3	43.6	45.5	32.6	46.4	0.623
Ca	74.8	71.4	76.9	74.2	70.0	84.9	78.0	65.0	87.7	90.3	70.0	110	0.719
Fe	1.88	1.59	3.00	2.02	1.24	3.42	1.99	1.63	2.69	3.35	1.92	3.51	0.775
Mn	0.083	0.034	0.149	0.082	0.019	0.098	0.050	0.022	0.156	0.022	0.021	0.221	0.304
Si	8.66	8.19	9.75	8.32	7.64	10.6	8.05	7.60	8.86	8.30	7.44	11.2	0.884
NH_3-N	1.21	0.14	2.83	1.07	0.17	2.43	1.60	0.25	3.23	2.31	0.46	9.09	0.688
TOC	2.29	0.70	5.51	1.80	0.70	3.61	3.20	1.13	4.40	2.18	0.69	7.01	0.907
HCO_3^-	456	380	519	443	380	529	487	405	523	433	375	616	0.967
F^-	0.326	0.275	0.397	0.326	0.283	0.380	0.337	0.269	0.434	0.339	0.255	0.464	0.919
Cl^-	3.80	1.30	20.2	3.20	2.30	7.25	7.60	2.30	32.9	2.70	1.13	23.3	0.700
SO_4^{2-}	<0.25	<0.25	25.10	<0.25	<0.25	43.3	0.30	<0.25	47.1	<0.25	<0.25	66.2	0.861
As(III) (μg/L)	5.72	<0.5	17.2	0.67	<0.5	18.5	9.99	1.23	29.3	18.0	1.00	107	0.455
As(V) (μg/L)	0.51	<0.5	1.20	<0.5	<0.5	1.87	<0.5	<0.5	1.02	0.74	0.45	5.99	0.534

Table 12. P values for rank sum results for Tazewell vs Champaign Counties for depth classes. Results in mg/L unless otherwise stated.
P values in bold indicate a significant difference (< 0.05).

	P			
Parameter	*Deep*	*Intermediate*	*Shallow*	*Glasford*
well depth (ft)	**0.041**	0.149	0.056	0.354
Dissol. As (μg/L)	0.246	0.984	**0.042**	0.435
Na	0.336	0.161	0.817	0.524
Mg	0.064	**0.008**	**0.009**	0.524
Ca	0.175	0.093	0.954	0.724
Fe	0.191	0.567	0.931	0.724
Mn	**0.005**	0.144	0.105	0.093
Si	0.109	0.890	0.132	0.833
NH_3-N	0.980	0.843	0.862	0.435
TOC	0.902	0.937	0.862	0.833
HCO_3^-	0.537	0.418	0.202	0.833
F^-	0.711	0.105	0.087	0.222
Cl^-	**0.011**	**0.015**	**0.001**	0.622
SO_4^{2-}	0.767	0.332	0.706	0.622
As(III) (μg/L)	0.109	0.417	**0.024**	0.284
As(V) (μg/L)	0.173	0.256	0.061	0.127
pH	0.921	0.859	0.977	0.724
ORP (mV)	0.639	0.797	0.622	0.524
SpC (μS cm^{-1})	0.604	0.649	0.817	0.724
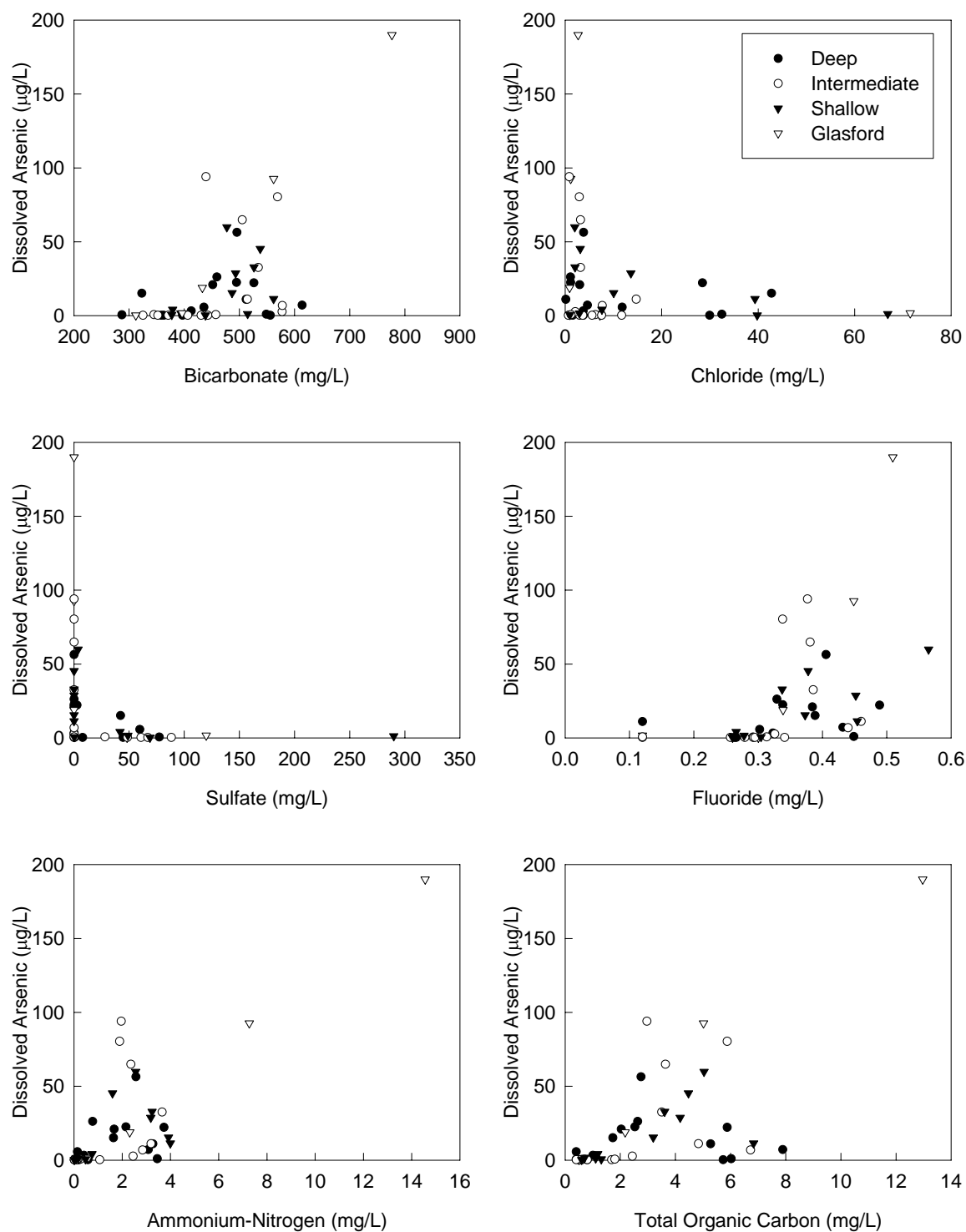
Figure 23. Dissolved arsenic versus bicarbonate, sulfate, fluoride, ammonium-N, and TOC for samples collected from private wells in Tazewell County.
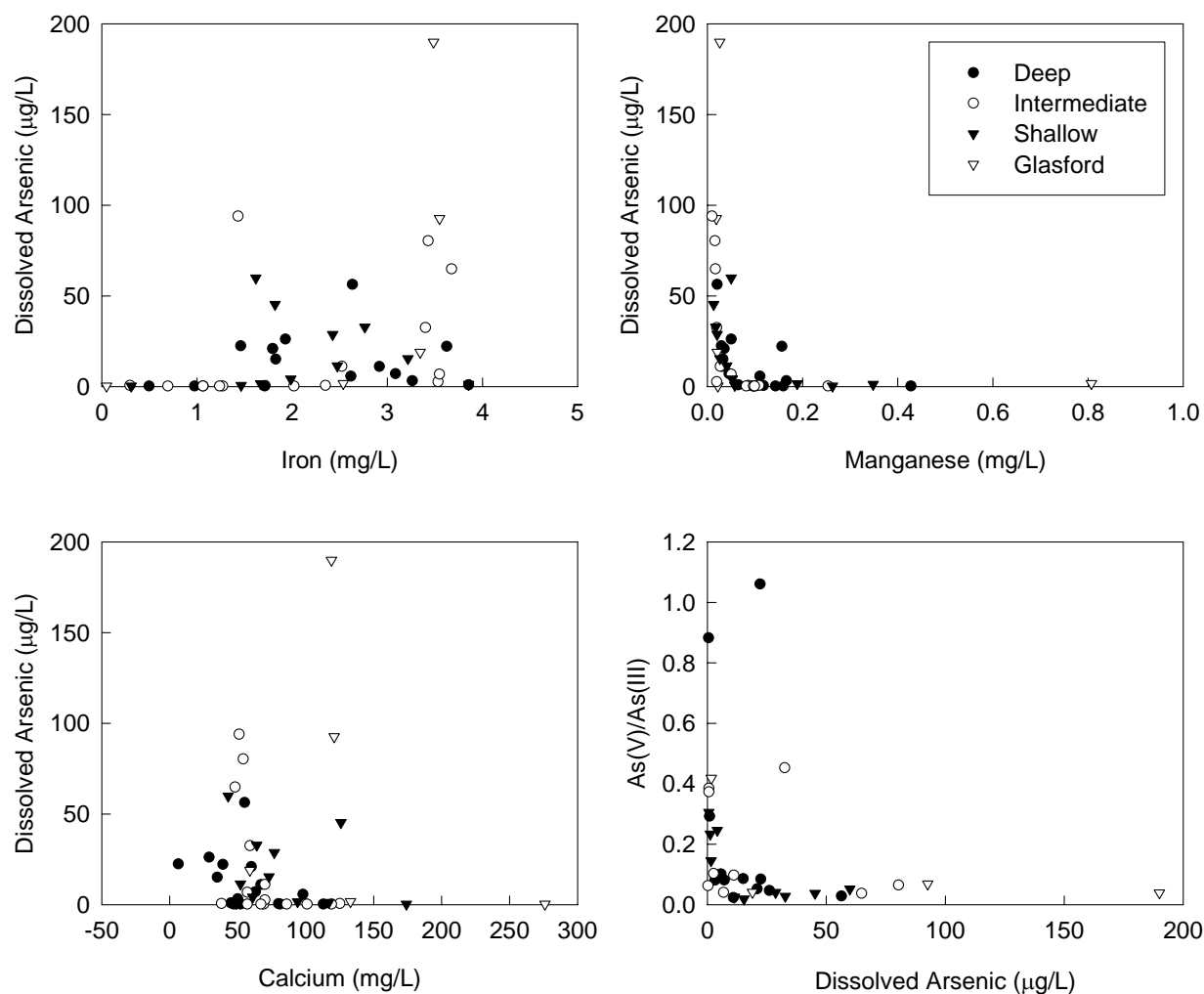
Figure 24. Dissolved arsenic versus iron, manganese, calcium, and As(V)/As(III) ratio for samples collected from private wells in Tazewell County.
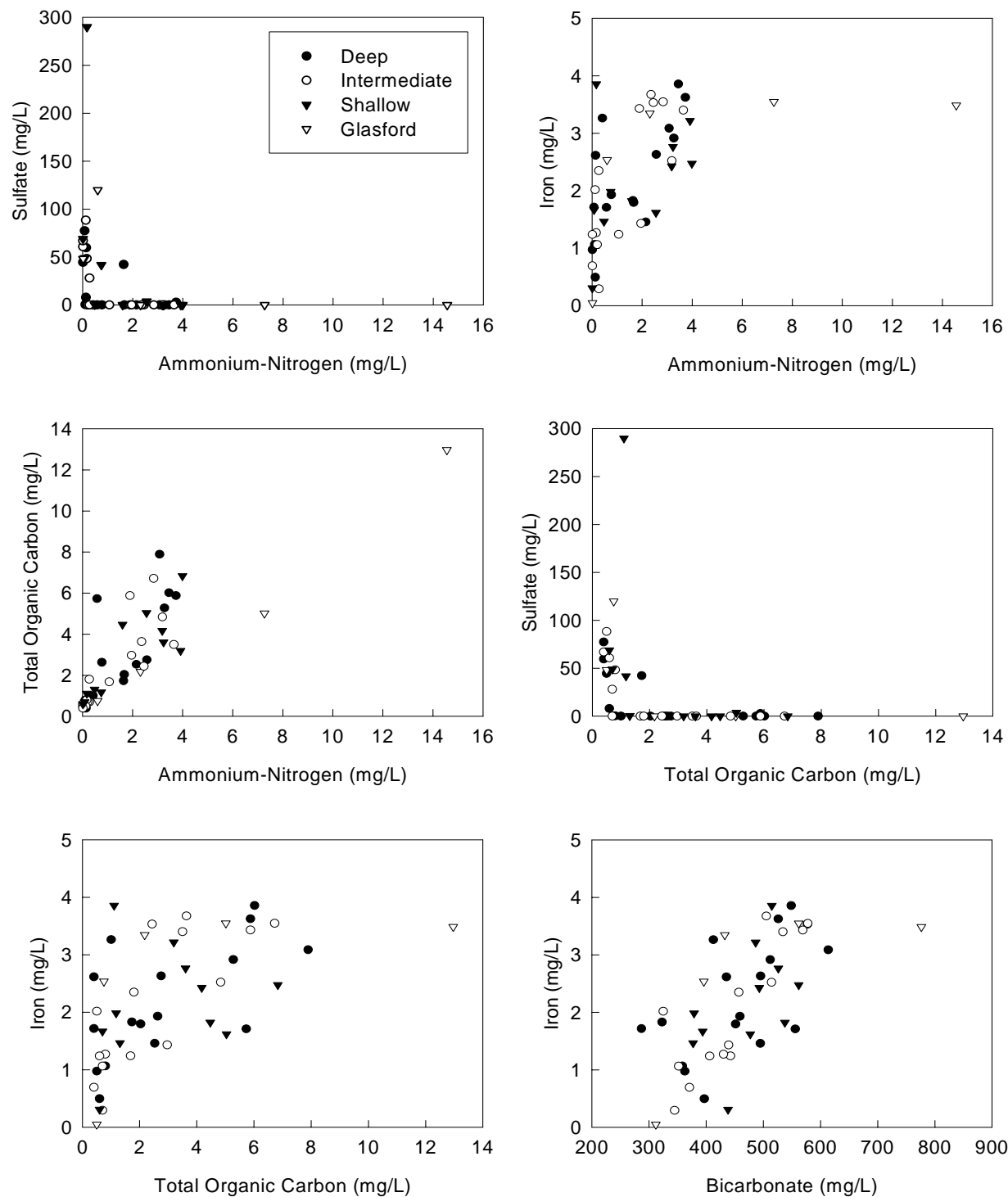
Figure 25. Relationships among various redox-sensitive parameters in the samples collected from private wells samples in Tazewell County.
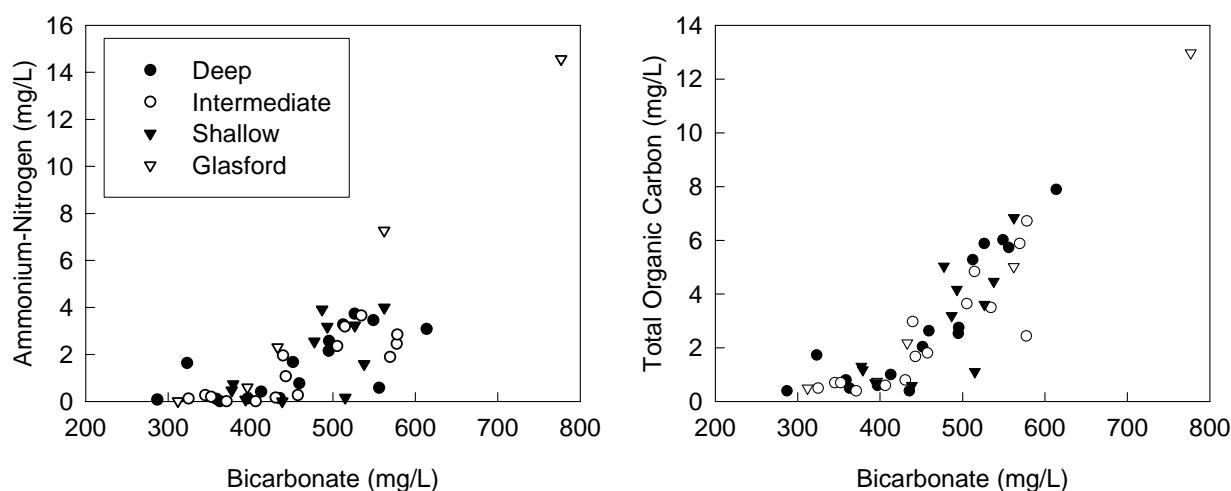
Figure 26. Relationships among various redox-sensitive parameters in the samples collected from private wells in Tazewell County (continued from Figure 25).

- NH$_3$-N concentrations tended to be mutually exclusive with respect to SO$_4^{2-}$ and Mn (i.e., when NH$_3$-N was present, SO$_4^{2-}$ and Mn were not and vice versa)
- TOC concentrations tended to be mutually exclusive with respect to SO$_4^{2-}$ and Mn
- elevated NH$_3$-N and TOC concentrations were found in samples with relatively elevated Fe
- NH$_3$-N and TOC were correlated
- Fe, NH$_3$-N, and TOC were correlated with HCO$_3^-$

Because SO$_4^{2-}$ concentrations appeared to have a bi-modal distribution (Figure 27), we examined arsenic relationships as a function of SO$_4^{2-}$ concentration. The data were divided into two groups: samples with SO$_4^{2-}$ < 10 mg/L (n = 32), and samples with SO$_4^{2-}$ greater than 28 mg/L (n = 15). Both groups contained wells from each depth interval. There were significant relationships for most of the chemical parameters from this grouping (Table 13 and Figure 28). Arsenic, Na, Fe, Si, NH$_3$-N, HCO$_3^-$, TOC, and F$^-$ all were significantly greater in the low-SO$_4^{2-}$ samples. Calcium, Mn, Cl$^-$, and ORP were significantly greater in the high-SO$_4^{2-}$ samples. The well depths were also greater for the low-SO$_4^{2-}$ samples.

Chemical Correlations in Champaign County
There were few correlations between arsenic and any other parameter (Figure 29; see also Figures B-2 and B-3 in Appendix B). There was a positive correlation between arsenic and

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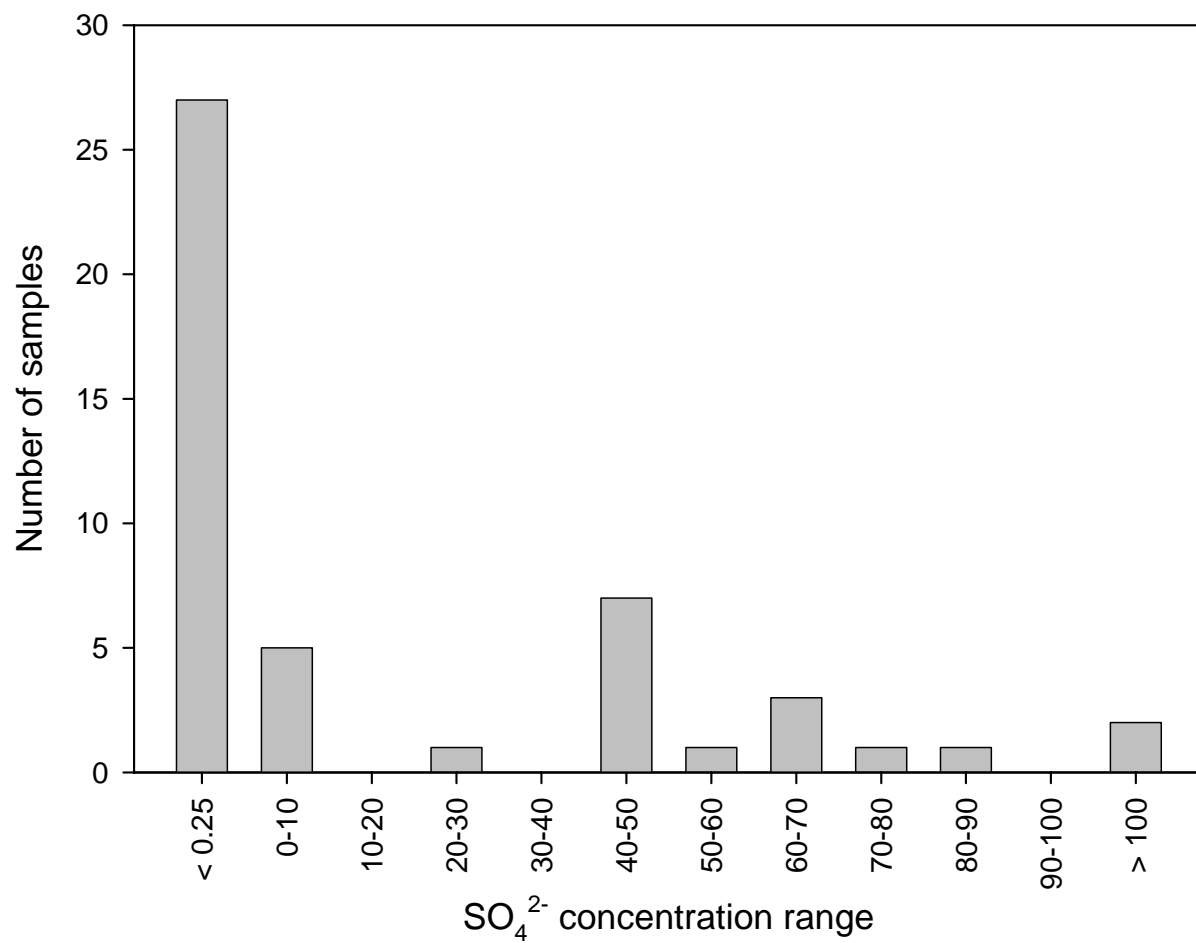
Figure 27. Distribution of sulfate concentrations for samples collected from private wells in Tazewell County.

Table 13. Rank sum test results comparing Tazewell County data as a function of SO_4^{2-} concentration.						
	$SO_4^{2-} < 10$ [n = 32]			$SO_4^{2-} > 28$ [n = 15]		
Parameter	*Median*	*25%*	*75%*	*Median*	*25%*	*75%*	*P*
well depth (ft)	215	172	282	146	106	218	**0.004**
As, d (Fg/L)	17.2	1.76	39.0	0.50	<0.5	1.62	**<0.001**
As(III), d (Fg/L)	12.1	1.65	36.1	0.58	<0.5	1.60	**<0.001**
As(V), d (Fg/L)	0.78	<0.5	1.94	<0.5	<0.5	0.52	**0.046**
Na	24.4	14.3	51.6	6.10	4.73	10.4	**<0.001**
Mg	38.0	34.1	41.4	35.3	32.0	41.6	0.592
Ca	74.2	67.8	78.1	85.1	73.3	97.1	**0.012**
Fe	2.58	1.67	3.42	1.67	0.760	2.01	**0.009**
Mn	0.033	0.020	0.076	0.109	0.086	0.237	**<0.001**
Si	9.06	8.22	10.8	7.65	7.26	8.20	**<0.001**
NH_3-N	2.41	0.92	3.26	0.120	<0.03	0.245	**<0.001**
TOC	3.56	2.11	5.51	0.60	0.50	0.79	**<0.001**
HCO_3^-	500	448	553	379	330	424	**<0.001**
F^-	0.38	0.33	0.45	0.29	0.26	0.30	**<0.001**
Cl^-	3.00	1.20	8.90	7.60	5.75	32.8	**0.003**
pH	7.27	7.16	7.39	7.14	6.94	7.25	**0.024**
ORP (mv)	57	49	70	98	80	124	**<0.001**
SpC (FS cm^{-1})	732	640	815	646	596	748	0.278

Notes:

Results in mg/L unless otherwise noted.

P values in bold indicate a significant difference (< 0.05).

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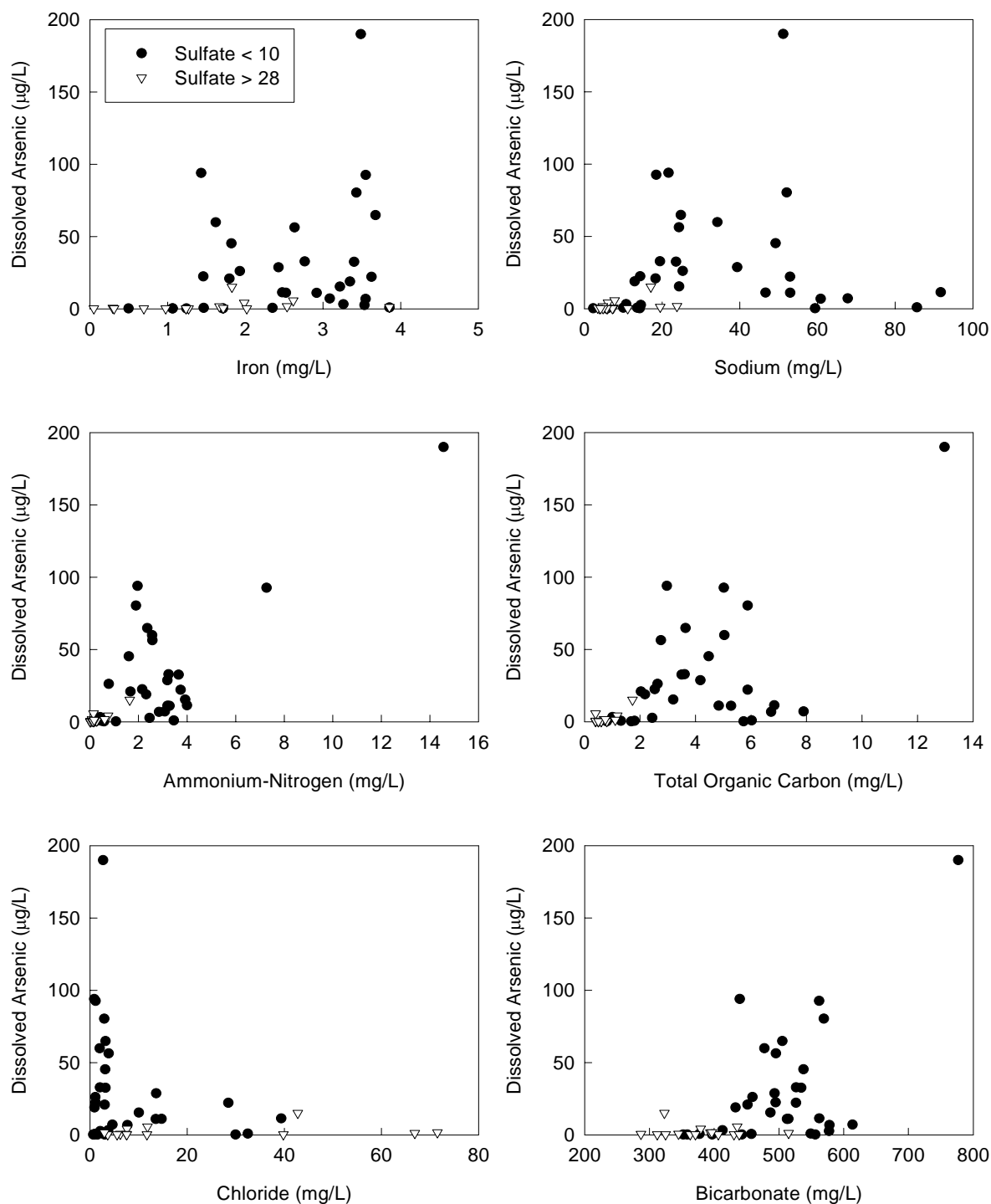
Figure 28. Dissolved arsenic concentrations versus iron, sodium, ammonium-N, TOC, chloride, and bicarbonate for samples collected from private wells in Champaign County and for two classes of sulfate concentration.
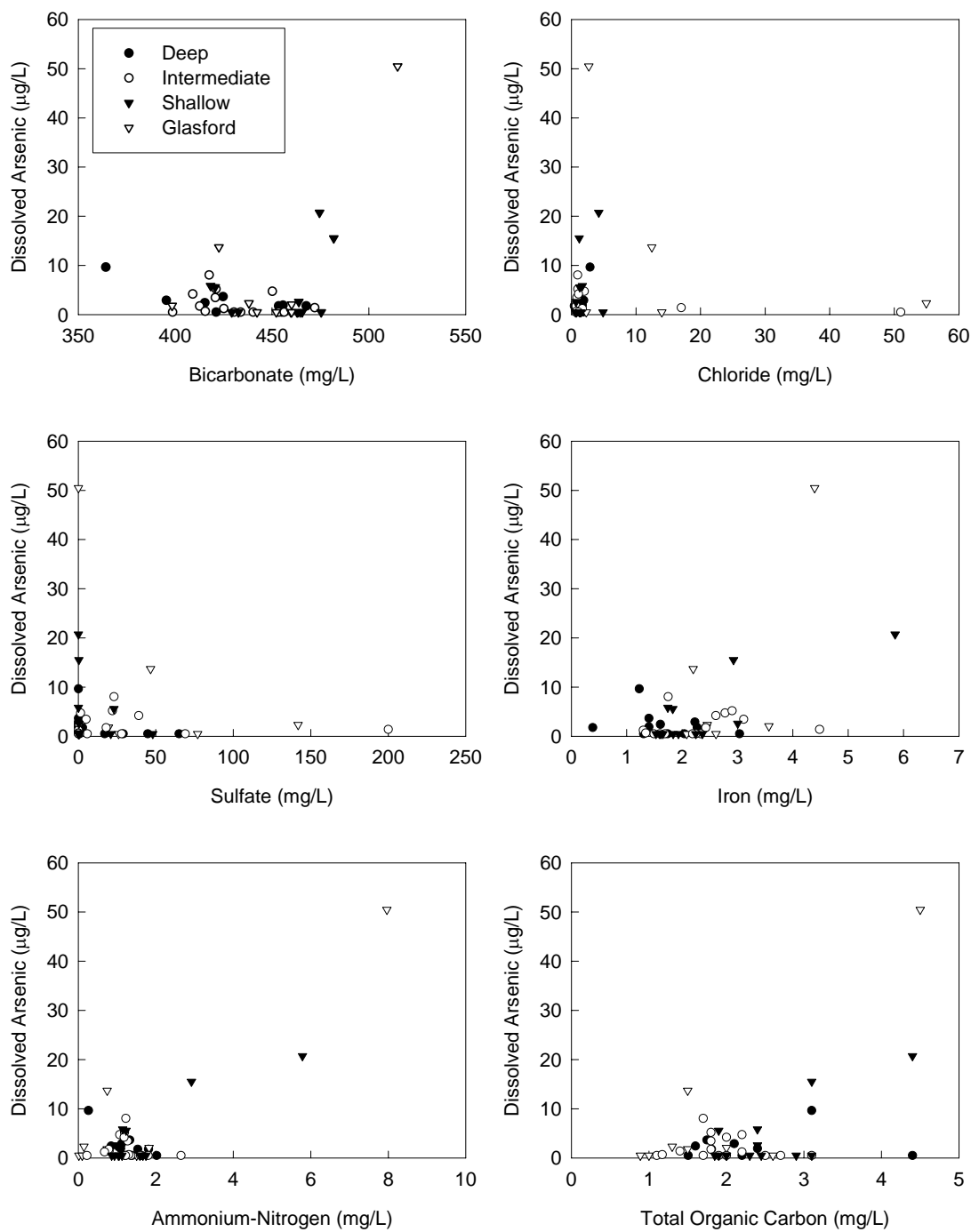
Figure 29. Relationships among various redox-sensitive parameters in samples collected from private wells in Champaign County.

NH$_3$-N ($r^2 = 0.75$). Higher arsenic concentrations (greater than 10 Ϝg/L) tended to have relatively high concentrations of HCO$_3^-$ and TOC, and no SO$_4^{2-}$. Other associations that were observed:

- Fe and Mn were positively correlated (slightly)
- SO$_4^{2-}$ and NH$_3$-N were mutually exclusive
- there was a positive correlation amongst NH$_3$-N, TOC, and HCO$_3^-$

Groundwater Geochemistry of Tazewell County

There were distinct differences in the groundwater chemistry north (groups 1-7) and south (groups 8-15) of the groundwater divide in Tazewell County (Figure 16). Concentrations of Na, HCO$_3^-$, and TOC were significantly greater in the north than the south (Table 14). Although the differences were not statistically significant, median concentrations of SpC, arsenic, NH$_3$-N, and Fe were greater in the north and SO$_4^{2-}$ was greater in the south. Differences in major ion chemistry can be seen in the Piper diagram, specifically the Na and SO$_4^{2-}$ concentrations (Figure 30). North of the divide, Na made up between 20 and 40% of the cation charge in most samples, while south of the divide Na made up 20% or less. Sulfate was undetectable in all samples collected north of the divide, but it comprised up to 40% of the anion charge in many samples collected south of the divide.

South of the groundwater divide, the chemistry from two groups of wells, those wells adjacent to the Mackinaw River (groups 8-11) and those up-gradient of the Mackinaw (groups 12-15), was compared. Along the Mackinaw River, the Mahomet Aquifer is unconfined, thus there is the possibility of a change in redox conditions in the groundwater that could affect arsenic concentrations. However, there were no statistically significant differences in chemistry between these two groups, although the median concentrations of SpC, SO$_4^{2-}$, Cl$^-$, NH$_3$-N, and TOC were greater and HCO$_3^-$ less in the up-gradient wells (groups 12-15).

Table 14. Rank sum test results for Tazewell County comparing wells north and south of the groundwater divide.						
	North; n=20			South; n=27		
Parameter	*Median*	*25%*	*75%*	*Median*	*25%*	*75%*	*P*
well depth (ft)	249	203	305	164	114	211	**<0.001**
Dissol. As (Ƒg/L)	6.97	0.415	25.4	4.19	<0.5	25.2	1.000
Na	47.9	7.95	56.2	14.4	7.28	23.1	**0.016**
Mg	38.2	34.2	42.0	35.7	33.8	41.4	0.755
Ca	75.6	67.8	86.7	74.5	70.4	83.6	0.780
Fe	2.46	1.57	3.46	1.93	1.29	3.11	0.287
Mn	0.054	0.027	0.120	0.050	0.021	0.110	0.863
Si	8.48	7.65	9.38	8.30	7.76	10.4	0.739
NH_3-N	2.37	0.24	3.36	0.77	0.13	2.35	0.109
TOC	4.93	1.06	5.95	1.68	0.60	2.72	**0.001**
HCO_3^-	521	418	562	438	373	493	**0.010**
F^-	0.405	0.272	0.453	0.326	0.286	0.376	0.212
Cl^-	4.15	1.95	14.4	3.80	2.10	7.60	0.906
SO_4^{2-}	<0.25	<0.25	0.35	3.80	<0.25	56.8	0.091
pH	7.16	7.00	7.29	7.26	7.17	7.36	0.168
ORP (mV)	60	51	90	67	52	100	0.598
SpC (ƑS cm^{-1})	771	662	848	647	612	735	0.063
As(III) (Ƒg/L)	6.17	0.46	18.9	3.24	<0.5	18.9	1.000
As(V) (Ƒg/L)	<0.5	<0.5	1.33	0.520	<0.5	1.21	0.613

Notes:

Results in mg/L unless otherwise stated.

P values in bold indicate a significant difference (< 0.05)
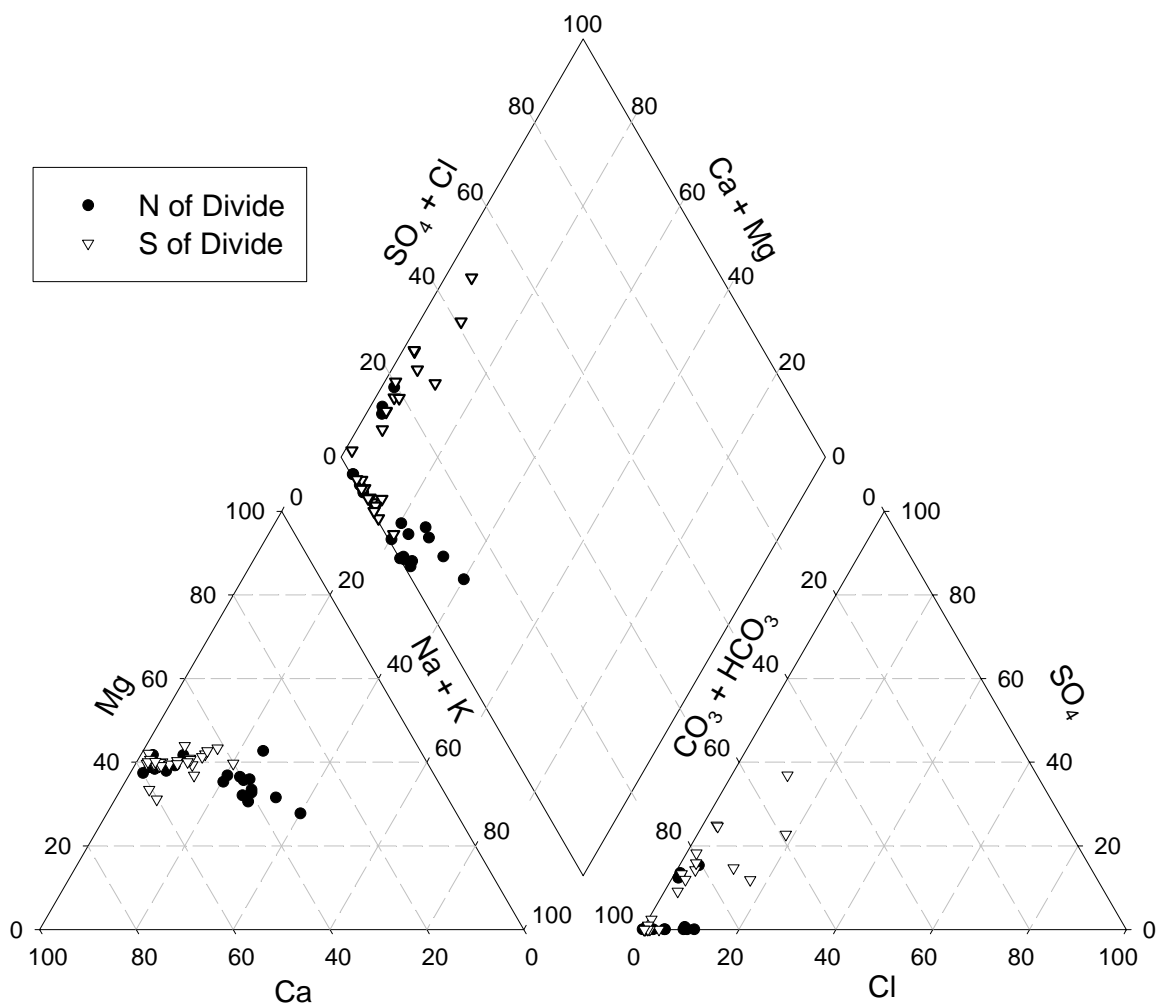
Figure 30. Comparison of relative concentrations of major ions north and south of the groundwater divide in Tazewell County.

DISCUSSION

Spatial Distribution of Arsenic

One of the notable features about arsenic groundwater concentrations in the Mahomet Aquifer is the high degree of spatial variability (Figures 13, 14). Wells with high concentrations of arsenic are often found close to wells with low concentrations. For example, two wells of almost identical depth less than 2.5 miles apart in Tazewell County had arsenic concentrations of 44 and 0.5 µg/L. These two wells also had significant concentration differences for other chemical species (SO_4^{2-}, HCO_3^-, TOC, NH_3-N). Four deep wells within five miles of one another had arsenic concentrations of 6, 16, 22, and 59 µg/L. Again, there were also differences in other chemical species among these wells (SO_4^{2-}, HCO_3^-, TOC, NH_3-N, Cl^-, Na).

This spatial variability in arsenic concentrations has been observed by other investigators where many samples were taken over a relatively small geographic area. For example, HOLM (1995) measured an arsenic concentration of 73 µg/L in a well in Tazewell County less than a mile from two other wells of similar depth with arsenic concentrations of 3 µg/L. The high-arsenic well also had higher concentrations of TOC and NH_3-N than the other wells. Data collected by HOLM (1995) also show the same mutual exclusion between arsenic and SO_4^{2-} as noted in the present work. The Mahomet wells sampled by WARNER (2001) and KELLY and WILSON (unpublished data, 2000 and 2002) were more widely distributed than in this study, but spatial variability in arsenic concentrations was also observed. Kelly and Wilson sampled a well that had an arsenic concentration of 266 µg/L within a half mile radius of four other wells of approximately the same depth that had arsenic concentrations between 17 and 30 µg/L. Large spatial variability in arsenic concentrations has also been reported in Wisconsin (SCHREIBER et al., 2000), New England (AYOTTE et al., 2003), Mexico (ARMIENTA et al., 2001), Argentina (SMEDLEY et al., 2002), and Bangladesh (NICKSON et al., 2000).

The depth of the well screen could be a critical factor in the arsenic concentration in the well water. For example, HARVEY et al. (2002) collected a number of water samples over a depth range of ~100 m in a core taken in Bangladesh. The highest dissolved arsenic concentrations (3.0-8.5 µM or 225-640 µg/L) were found at intermediate depths (30-50 m), while lower concentrations were found near the surface (<< 1 µM or 75 µg/L) and at 80-100 m (~0.5 µM or 38 µg/L). In Tazewell County, the greatest arsenic concentrations in the Mahomet Aquifer were found in wells screened in the intermediate part of the aquifer, although the difference with respect to the other depth locations was statistically insignificant (see Table 8).

The large spatial variability in arsenic concentrations, as well as many other chemical species, indicates that the Mahomet Aquifer is not "well mixed." The water chemistry is a function of the chemistry of the water recharging the aquifer and of rock-water interactions (e.g., mineral precipitation and dissolution, adsorption/desorption, microbially mediated oxidation-reduction reactions). These rock-water interactions are controlled by the geology and hydrogeology of the aquifer. Differences in hydraulic conductivity, mineralogy and petrology, and the presence or absence of organic-rich deposits, among other things, determine what reactions will occur. The Mahomet Aquifer is not a homogeneous sand deposit with uniform conductivity. There are

numerous, generally discontinuous, low-permeability deposits (silts and clays) and organic-rich zones that were deposited with the sands and gravels.

It appears that arsenic may be particularly sensitive to geochemical conditions in the Mahomet Aquifer. Its correlation with redox-sensitive species such as SO_4^{2-}, HCO_3^-, TOC, and NH_3-N indicate that redox conditions are likely controlling the aqueous concentration of arsenic. High TOC and NH_3-N concentrations suggest buried organic-rich zones nearby, and that there is active degradation of organic matter. Elevated HCO_3^- concentrations are likely primarily due to the production of CO_2 during organic carbon degradation. Iron oxyhydroxide minerals would be expected to dissolve and release Fe^{2+} into solution, and any arsenic associated with these minerals would also be released into solution.

Although arsenic in Mahomet groundwater probably desorbed from aquifer sediments, it does not appear to have migrated great distances because there are no obvious "plumes" of arsenic-contaminated groundwater on the scale that we sampled. Assuming these reactions have been occurring for thousands of years, it is apparent that arsenic is being severely retarded, i.e., removed from solution down-gradient from its sources. Mechanisms for removal include adsorption and precipitation of secondary minerals.

Arsenic Geochemistry

Relationships between Arsenic and Other Solutes
There have been a number of studies of arsenic in aquifers throughout the world. Other chemical parameters are typically measured, and arsenic has been observed to correlate with different parameters depending on hydrogeological and geochemical conditions.

Aquifers in Arizona (ROBERTSON, 1989) and Argentina (SMEDLEY et al., 2002), that have elevated arsenic have a different geochemistry than those in more humid regions, including the Mahomet and Glasford Aquifers. Aquifers in arid regions tend to be oxygenated and have relatively elevated pH values (7.5 - 9.3). The arsenic in these aquifer systems is predominantly As(V), which is in the anionic form ($H_2AsO_4^-$/$HAsO_4^{2-}$) in this pH range. In these two studies, arsenic was correlated with anions such as F^- and HCO_3^-, with vanadium and molybdenum, which were most likely in anionic forms ($H_2VO_4^-$/HVO_4^{2-}, MoO_4^{2-}), and with pH. The authors hypothesized that the correlation of As(V) with other anions and pH was due to sorption to iron oxyhydroxides and that sorption was therefore a significant control of arsenic concentrations in these groundwaters. We also saw a correlation between arsenic and F^- in the Tazewell County samples (Figure 23), although most of the arsenic was present as As(III) rather than As(V).

The pH in these aquifers was relatively high compared to most aquifers in humid zones. In our study, the maximum pH was 7.84, 91% of the samples had a pH between 6.5 and 7.5, and we did not observe a correlation between pH and arsenic concentrations. For an increase in the pH between 6.5 and 7.5, the increase in arsenic solubility is relatively small (KIM et al., 2000), and it would be difficult to determine if pH was the controlling variable. The increase in arsenic solubility is much greater at pH values greater than 8.0.

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ARMIENTA et al. (2001) sampled an aquifer in Mexico contaminated with arsenic in a geological setting much different than the Mahomet Aquifer. The aquifer was a fractured limestone, but influenced in some areas by hydrothermal activity and groundwater temperatures were elevated in some areas (> 28EC). The wells with the highest arsenic concentrations (> 500 Ｆg/L) had by far the lowest ORP values, but other wells with elevated arsenic (> 50 Ｆg/L) did not have relatively low ORP values. Arsenic was not correlated with pH, Fe, or SO_4^{2-}. Arsenopyrite (FeAsS) oxidation was determined to be the source of arsenic.

The most extensive studies on the source and fate of arsenic in groundwater have been done in the shallow aquifers in Bangladesh and eastern India. The polluted groundwater is coming from organic-rich deltaic sediments, with highest concentrations in deeper, more reduced sections of the aquifers. Investigators have reported different chemical correlations with arsenic. Arsenic and iron have been found to be associated in the solid phase (HARVEY et al., 2002; MCARTHUR et al., 2001; NICKSON et al., 1998; NICKSON et al., 2000), and sometimes in solution (DOWLING et al., 2002; NICKSON et al., 1998; NICKSON et al., 2000) but sometimes not (MCARTHUR et al., 2001; NICKSON et al., 1998; NICKSON et al., 2000). In most cases, arsenic was correlated with HCO_3^- (HARVEY et al., 2002; MCARTHUR et al., 2001; NICKSON et al., 1998; NICKSON et al., 2000). The correlation with HCO_3^- was determined to be due to reductive dissolution of iron oxyhydroxides coupled with oxidation of abundant organic matter in the sediments. The arsenic, either adsorbed to or co-precipitated with FeOOH, is released into solution, and HCO_3^- is produced from the oxidation of the organic carbon. We also saw an association between arsenic and HCO_3^- in the Tazewell County samples, and the above explanation probably explains some processes in the Mahomet Aquifer.

While it is clear that there must be some relation between iron and arsenic, we did not observe that they were correlated in solution. There may be several reasons for this, as suggested by MCARTHUR et al. (2001): (1) dissolved Fe may also come from weathering of minerals in addition to FeOOH; (2) the Fe/As ratio in dissolving FeOOH is variable; and (3) Fe may be removed from solution into Fe minerals such as vivianite ($Fe_3(PO_4)_2$), siderite ($FeCO_3$), or pyrite.

In Bangladeshi samples, arsenic was also observed to be correlated with NH_3-N, methane (CH_4), dissolved organic carbon (DOC), and Ca (DOWLING et al., 2002; HARVEY et al., 2002). Arsenic was not found where DO or nitrate were present (NICKSON et al., 1998; NICKSON et al., 2000). RAVENSCROFT et al. (2001) and HARVEY et al. (2002) observed that arsenic and SO_4^{2-} tended to be mutually exclusive, and SO_4^{2-} was absent from the samples collected by DOWLING et al. (2002). We also observed that arsenic was correlated with NH_3-N and TOC. Although we did not measure CH_4, it seems reasonable it would be correlated with arsenic. Methane has been detected in many parts of the Mahomet Aquifer and overlying formations. MEENTS (1960) reported that the source of the CH_4 was degradation of organic matter, either in the Sankoty (Mahomet) sand or buried soils, peats, and organic-rich silts associated with interglacial stages, especially the Sangamon soil, which overly the Mahomet.

The mutual exclusivity of arsenic and SO_4^{2-} (and Fe and SO_4^{2-}) was used by RAVENSCROFT et al. (2001) as evidence that pyrite oxidation was not the source of arsenic in Bangladeshi groundwater. We observed that arsenic concentrations in Tazewell County were significantly

greater in samples that had low concentrations of SO_4^{2-} indicating that pyrite oxidation was not the source of arsenic. In addition, elevated concentrations of NH_3-N and Fe and lower ORP values were found in these samples, suggesting strongly reducing conditions.

We initially hypothesized that SO_4^{2-} reducing conditions might actually reduce the solubility of arsenic by promoting the precipitation of arsenic-containing sulfide solid phases. In a subsequent study, KIRK et al. (in press) sampled a subset of the wells from this study and detected significant volumes of methane in many of the wells that had elevated arsenic. Based upon these and other observations, they concluded that arsenic concentrations are only elevated where SO_4^{2-} has been exhausted and is no longer available as an electron acceptor. If SO_4^{2-} is present and SO_4^{2-} reduction is active, arsenic concentrations are low because any arsenic entering solution is probably removed by precipitation as an arsenic sulfide mineral or by coprecipitation with other sulfide minerals. After SO_4^{2-} has been eliminated, methanogenesis becomes the dominant metabolism and arsenic, in the absence of a precipitation pathway, builds up in the groundwater. In addition, based upon the relationship between arsenic, hydrogen gas, and other redox sensitive species, KIRK et al. (in press) suggested that some degree of iron reduction may be occurring in zones dominated by both methanogens and SO_4^{2-} reducers.

Our data suggest that the availability of OM may be driving the reducing conditions that cause depletion of SO_4^{2-}. Low levels of SO_4^{2-} tended to occur where TOC concentrations were high. KIRK et al. (in press) observed that wells with significant methane only occurred where TOC exceeded 2 mg/L, while those with TOC below this level had significant concentrations of SO_4^{2-}. The rate at which terminal electron acceptors are used up in pristine groundwater environments is often limited by the supply of organic substrates (CHAPELLE, 1993; POSTMA and JAKOBSEN, 1996). Hence, areas richer in OM are more likely to have exhausted the supply of SO_4^{2-}, thus allowing accumulation of arsenic.

As discussed above, significantly greater concentrations of HCO_3^- in these samples are likely due to CO_2 as a result of OM oxidation during reductive dissolution of ferric oxyhydroxides. In addition to driving reductive iron dissolution, organic ligands may bind with arsenic in solution and also decrease the amount of adsorption of arsenic (REDMAN et al., 2002).

The study most relevant to the present one is that of WARNER (2001), who sampled in the Mahomet Aquifer, although in that study fewer samples were collected over a much larger area. WARNER (2001) found that arsenic was correlated with depth, Cl^-, barium, and molybdenum, and not with Fe. WARNER (2001) may have seen the same relationship between arsenic and SO_4^{2-} that we saw, although it is not possible to tell from the published data. The correlation with Cl^- suggested that there was a deep bedrock source of arsenic. We did not observe this correlation in the Tazewell County samples; in fact, samples with high arsenic tended to have low Cl^- concentrations. However, results from Piatt, Macon, and DeWitt Counties collected by Kelly and Wilson in 2000 and 2002 are generally in agreement with Warner's results, i.e., arsenic was somewhat correlated with Cl^- and dissolved solids, with highest concentrations along the valley walls where there is recharge from highly mineralized bedrock waters.

In the Tazewell County samples, the highest arsenic concentrations were either in the intermediate zone of the Mahomet aquifer or the Glasford aquifer. If the bedrock was the source, then the deep Mahomet wells should have the highest concentrations. If the till between the Glasford and the Mahomet was the source, then the shallow Mahomet samples should have higher concentrations than the intermediate samples. This is further evidence that the predominant source of arsenic in the Mahomet Aquifer is from iron oxyhydroxides in the sand.

Geochemical Modeling

Saturation indices were calculated for the water samples for Tazewell County to determine potential solubility controls on Fe and Mn. Redox conditions were controlled by the field-measured ORP in the calculations. All samples were supersaturated with respect to crystalline ferric oxide minerals (hematite, goethite). Most of the samples were undersaturated with respect to amorphous ferric oxyhydroxide ($Fe(OH)_3$) and slightly oversaturated or near saturation with respect to the ferrous carbonate mineral siderite ($FeCO_3$). All samples were strongly undersaturated with respect to pyrite; however, if the H_2S concentration was set to the threshold concentration for odor detection by smell (0.025 to 0.25 $\mu g/L$), almost all of the samples were saturated or supersaturated with respect to pyrite.

All of the samples were undersaturated with respect to rhodochrosite ($MnCO_3$), pyrolusite (MnO_2), and manganite ($MnO(OH)$). Most of the samples were slightly oversaturated or near saturation with respect to calcite ($CaCO_3$).

Although the modeling results indicated that all of the water samples from Tazewell County were supersaturated with respect to crystalline iron oxides, the abundant Fe in solution indicates that Fe reduction occurs in the aquifer. The ORP measured in the field apparently did not reflect the iron equilibria. There may not have been sufficient Fe^{3+} in solution, and a redox pair other than Fe^{3+}/Fe^{2+} may therefore have been controlling the measured ORP. The ORP should probably have been lowered to more realistically model the iron system. However, decreasing the ORP of the samples would not significantly affect the siderite saturation indices (SI).

Because most of the samples had SI values for siderite close to equilibrium (98% |SI| < 1, 63% |SI| < 0.5), it appears that siderite may be an important control on iron solubility. Most of the samples (71%) had positive SI values, indicating siderite would be favored to precipitate out of solution. The production of CO_2 (HCO_3^-) from degradation of OM would favor siderite precipitation. The largest siderite SI values were for samples with no SO_4^{2-} and the greatest arsenic concentrations were found in low SO_4^{2-} samples. Therefore if siderite is precipitating out of solution it is apparently not removing arsenic from solution. This is supported by the fact that almost all of the samples that were undersaturated with respect to siderite had arsenic concentrations less than 2 $\mu g/L$, and almost all of the samples oversaturated with respect to siderite had arsenic concentrations greater than 10 $\mu g/L$ (Figure 31).

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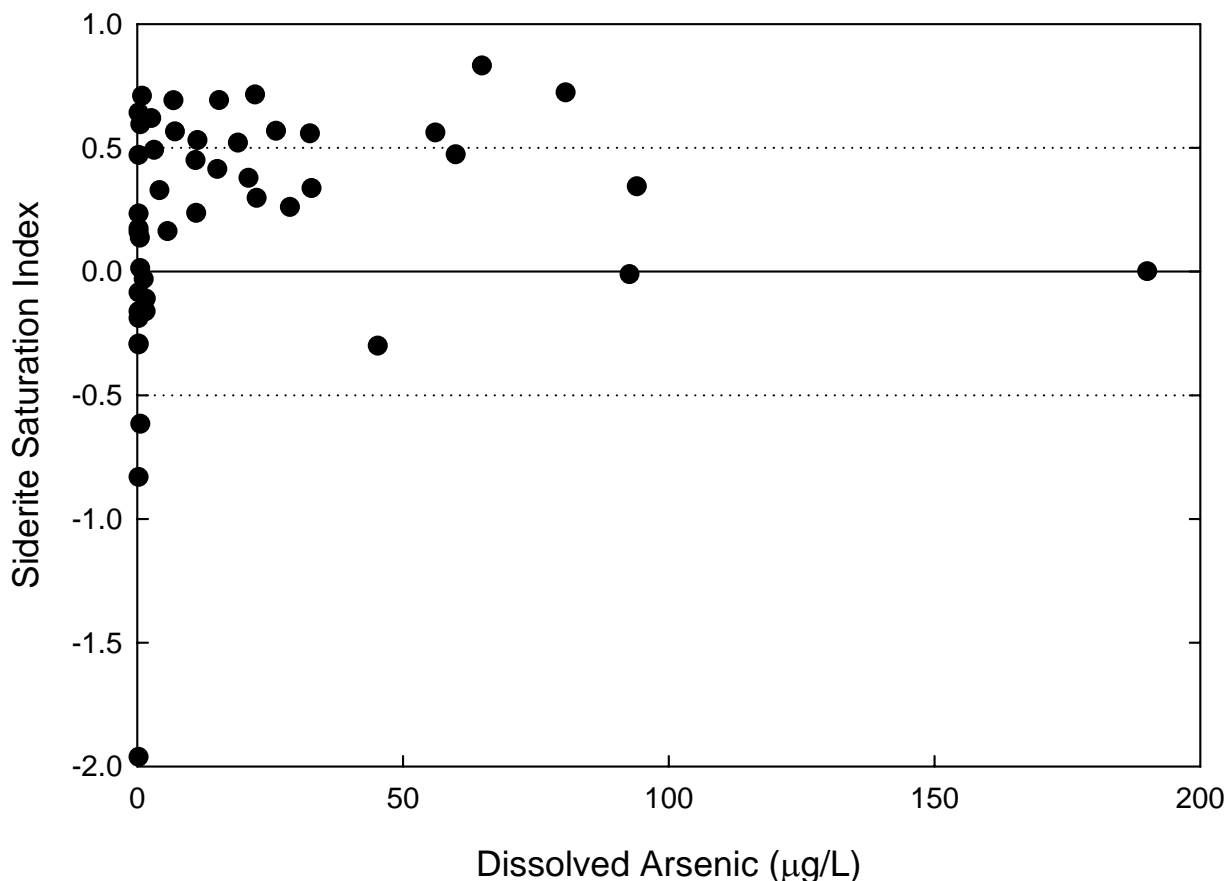
Figure 31. Siderite saturation indices (SI) versus dissolved arsenic for samples collected from private wells in Tazewell County. SI = 0 indicates thermodynamic equilibrium. SI values between -0.5 and 0.5 are assumed to be at equilibrium.

Arsenic Speciation

Both As(III) and As(V) were detected in most samples, but the main arsenic species in both Champaign and Tazewell Counties was As(III). This was not surprising, considering the strongly reducing conditions in the aquifer. In most samples with at least 10 μg/L arsenic, As(V) comprised less than 15% of the total (Figures 18 and 32). WARNER (2001) found similar arsenic speciation in groundwater samples from DeWitt, Logan, and McLean Counties, which are between Champaign and Tazewell Counties. For 6 out of 10 samples, As(V) comprised less than 15% of the total arsenic (Figure 32). An earlier study (HOLM and CURTISS, 1989) that included several community wells in the Mahomet Aquifer also found that both arsenic species were detectable.

In most published studies of arsenic speciation, both As(III) and As(V) were found and the less abundant species was at least 2% of the total arsenic. MATISOFF et al. (1982) found that As(III) and As(V) concentrations were approximately equal in groundwater samples from a sandstone and a sand-and-gravel aquifer in Ohio. DELRAZO et al. (1990) sampled 128 wells in northern
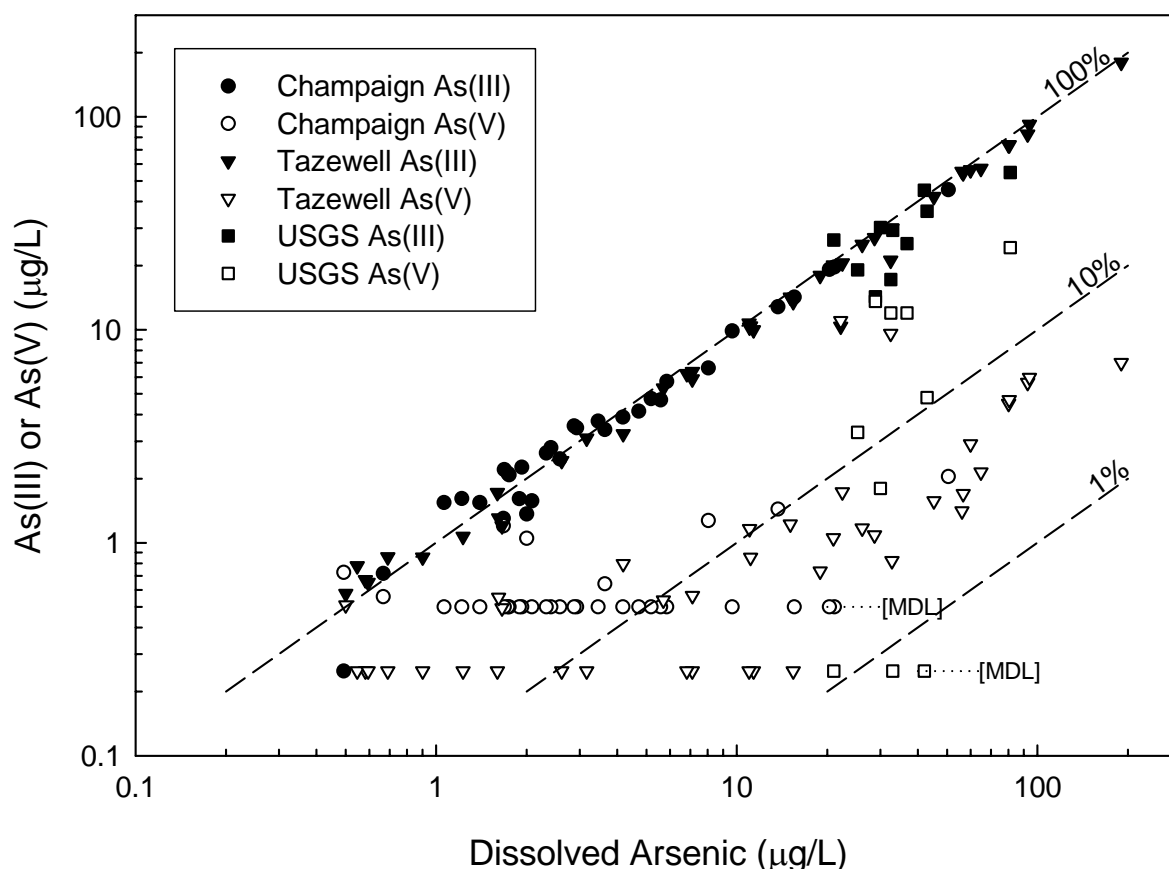
Figure 32. Concentrations of As(III) and As(V) versus dissolved arsenic for samples from the Mahomet and Glasford Aquifers. Data labeled "Champaign" and "Tazewell" are from private wells sampled in this study. Data labeled "USGS" are from WARNER (2001). Dashed lines represent the fraction of As(III) or As(V) (1, 10, or 100%) of the dissolved arsenic. MDL represents detection limits for arsenic (0.5 µg/L for Champaign, 0.25 µg/L for Tazewell and USGS).

Mexico and found that As(V) was at least 50% of total arsenic in 109 samples and less than 20% in 4 samples. SMEDLEY (1996) and SMEDLEY et al. (1996) studied well water in a gold mining area of Ghana and found that for wells with no detectable DO, As(V) was 70-97% of total arsenic, while for wells with detectable DO As(III) was undetectable. WELCH et al. (1988) reviewed previously unpublished USGS arsenic speciation data for wells in the western U.S. For 7 of 9 wells, the As(V):As(III) ratio was between 0.2 and 0.6. For one well the ratio was 12.5 and for the other well it was 0.03. FICKLIN (1983) analyzed water from 9 irrigation wells in Utah and found that As(V) made up 23-~100% of the total arsenic. BOYLE et al. (1998) found that for Bowen Island, British Columbia, the As(III):As(V) ratio varied from 0.2 to 100. YAN et al. (2000) found that As(III):As(V) was between 0.02 and 1 in the reduced zone of a glacial till in Saskatchewan and between 1 and 10 in redox transition zones above and below the till. CHEN et

al. (1995) found that for the endemic blackfoot disease area of Taiwan the average As(III) and As(V) concentrations were 462±129 and 177±109 μg/L, while for a control area with no blackfoot disease the average concentrations were 572±42 and 38±18. HUNG and LIAO (1996) found that As(V) made up 92% of the total arsenic in two wells in Taiwan. KONDO et al. (1999) found that for 6 wells in Fukoka Prefecture, Japan, the As(III):As(V) ratio was 0.07 to 3.2.

Publications in which measurements of either As(III) or As(V) were below detection limits in most or all samples were less common than those that reported both species. KORTE (1991) found that As(III) was the only detectable species in shallow wells in an alluvial aquifer in Missouri. On the other hand, ROBERTSON (1989) found that As(V) was the only species that was detectable in wells in alluvial basins in Arizona. RAESSLER et al. (2000) collected 4 samples from 4 wells near Kelheim, Germany, at roughly 3-month intervals and found that for three of the wells As(V) was the only species that was ever detected and that for the other well As(III) was detected only twice.

In the present study neither MMAA nor DMAA was detected in any sample. This is consistent with some published studies. Both MMAA and DMAA were undetectable in well water from Taiwan (CHEN et al., 1994; IRGOLIC, 1982) and Japan (KONDO et al., 1999). Other researchers have found one or both methylated species in well water from Taiwan (LIN et al., 1998), Mongolia (LIN et al., 2002), Mexico (DELRAZO et al., 1990), and West Bengal (SHRAIM et al., 2002). Methylated arsenic species have been found in groundwater that was affected by gross contamination by arsenical herbicides (HOLM et al., 1979; HOLM et al., 1980) or by both inorganic arsenic and organic waste (DAVIS et al., 1994).

There have been few reports of colloidal or particulate arsenic in groundwater. EDWARDS et al. (1998) found that for groundwater samples from 26 water treatment plants particulate arsenic made up 18 percent of the total arsenic on average. This is somewhat higher than but comparable to the results of the present work (Figure 20). EDWARDS et al. (1998) also reported 50-60 percent arsenic removal from a surface water sample by a 0.02 μm filter, but not for any groundwater samples.

Arsenic Speciation in Relation to Oxidation-Reduction Conditions
FERGUSON and GAVIS (1972) constructed Eh-pH diagrams for arsenic speciation at 25EC. The portion of the diagram that includes the pH and ORP values of the Mahomet Aquifer was recalculated for 14EC, the approximate temperature of the aquifer (Figure 33). Thermodynamic data for temperature adjustments was taken from NORDSTROM and ARCHER (2003).

The diagonal lines separating the As(V) and As(III) species in Figure 33 were calculated as follows. The half-reaction for the reduction of As(V) to As(III) is given by equation 2.

$$H_3AsO_4 + 2H^+ + 2e^- = H_3AsO_3 + H_2O \tag{2}$$
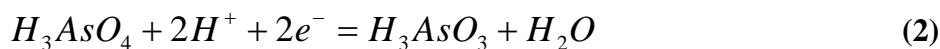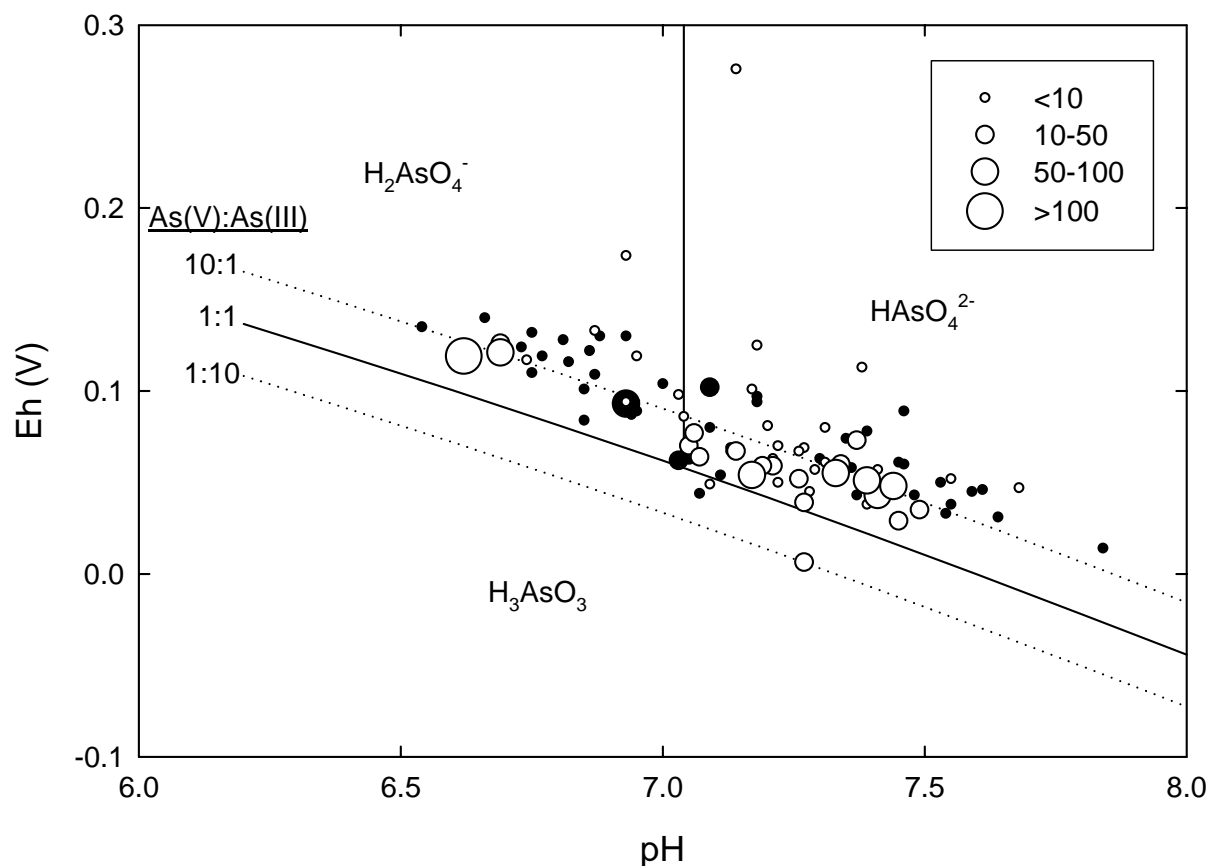
Figure 33. Arsenic Eh-pH diagram, 14EC. Size of symbols indicates dissolved As concentration in Ｆg/L. Filled symbols Champaign County, open symbols Tazewell County. Dotted lines indicate shift in stability fields for different As(V):As(III) ratios.

The Nernst equation (equation 3) relates the arsenic species concentrations at equilibrium.

$$E = E^0 + k\left(Log_{10}\left(\frac{[H_3AsO_4]}{[H_3AsO_3]} \right) - 2pH \right) \tag{3}$$

In equation 3, E^0 and k are a constant and a collection of constants, respectively. In the pH range of the Mahomet Aquifer, H_3AsO_4 makes up a small fraction of the As(V), which is given by equation 4 (Stumm and Morgan, 1996).

$$\alpha^V = \frac{[H_3AsO_4]}{As(V)} = \frac{1}{1 + K_{a1}10^{pH} + K_{a1}K_{a2}10^{2pH} + K_{a1}K_{a2}K_{a3}10^{3pH}} \tag{4}$$

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A similar equation can be derived for the fraction of As(III) in the H_3AsO_3 form (α^{III}). Essentially all of the As(III) is in the H_3AsO_3 form. Substituting equation 4 into equation 3 gives equation 5, which relates the equilibrium redox potential to the pH and concentrations of As(V) and As(III) (measured quantities).

$$E = E^0 + k\left(Log_{10}\left(\frac{As(V)\alpha^V}{As(III)\alpha^{III}} \right) - 2pH \right)$$ (5)

The lines labeled 1:1, 10:1, and 1:10 in Figure 33 are for the different ratios of As(V) to As(III) used in equation 5. The measured pH and ORP values, the points in Figure 33, plot in areas for which both As(III) and As(V) should be detectable and, indeed, both species were detectable in most samples (Tables A1 and A2, Figure 19). However, most of the points in Figure 33 lie in the As(V) field, the area in which As(V) makes up more than 50% of the total arsenic, whereas As(III) made up at least 85% of the arsenic in most of the samples analyzed in the present work. Other researchers have also found that their pH-ORP data plot completely in the As(V) field (ARMIENTA et al., 2001; BOTTOMLEY, 1984; PLANER-FRIEDRICH et al., 2001; ROBERTSON, 1989; SMEDLEY, 1996; WELCH et al., 1988). SMEDLEY (1996) reported groundwater analyses for which As(III) made up 3-39% of the total arsenic, the ORP values were 221-469 mV, and the pH values were between 5.4 and 7.2. Although many of these data would be off the top of the scale of Figure 33, both arsenic species were detectable.

The only As(III) species considered in equation 5 are H_3AsO_3 and $H_2AsO_3^-$, so the value of α^{III} was close to 1.0 for all measured pH values. However, there is evidence for complexation of As(III) by carbonate ions (KIM et al., 2000; LEE and NRIAGU, 2003). The alkalinity values in the Mahomet Aquifer are fairly high ($10 mmol/L), so if the As(III)-HCO_3^- stability constants are large enough, α^{III} could be significantly less than 1.0. An α^{III} value of 0.1 would shift the As(III)-As(V) boundary up approximately 30 mV and many more points would plot in the As(III) field.

Arsenic Removal at Water Treatment Plants
Table 15 presents the water treatment methods at the treatment plants. All plants except Mason City used some form of aeration. Some plants also used prechlorination or potassium permanganate addition ($KMnO_4$) to oxidize soluble ferrous iron to insoluble ferric iron. All plants but Mason City filtered their water. All plants fluoridated their water. Four plants used ion exchange softening. Two plants, Kenney and Mason City, added polyphosphates, probably to inhibit iron oxidation ("red water") or $CaCO_3$ precipitation ("scaling").

Figure 34 compares arsenic removal at the treatment plants. Only one well was operating at the time of sampling at DeWitt, Goodfield, Kenney, McLean, Monticello, and Morton. Neither of the Cisco wells was operating at the time of sampling. The operator turned each well on to allow sampling, but the treated water was taken from the water tower and it was not known if the water had been from one or both of the wells. The arsenic concentrations of all operating wells are shown.

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Table 15. Water treatment methods in use at treatment plants that use Mahomet Aquifer water.									
	Aeration[a]	Prechlorination	KMnO$_4$	Coagulation	Filtration[b]	Disinfection[c]	Fluoridation	Softening	Polyphosphate[d]
Cisco	F				P	O	c	c	
Clinton	G	c			P	C	c		
Danvers	F				P	C	c	c	
DeWitt	F		c	c	P	C	c		
Goodfield	F	c			P		c		
Kenney	G				P	C	c		B
Mason City						C			S
McLean	F	c			P		c		
Monticello	F	c			P		c	c	
Morton	F	c	c		M	C	c	c	

Notes:

c Process is used. Blank indicates process is not used.
a F is forced draft aeration, G is gravity tray aeration.
b P is pressure sand filtration, M is Manganese greensand filtration.
c O is ozone, C is chlorination.
d B is blended phosphate, S is sodium polyphosphate.

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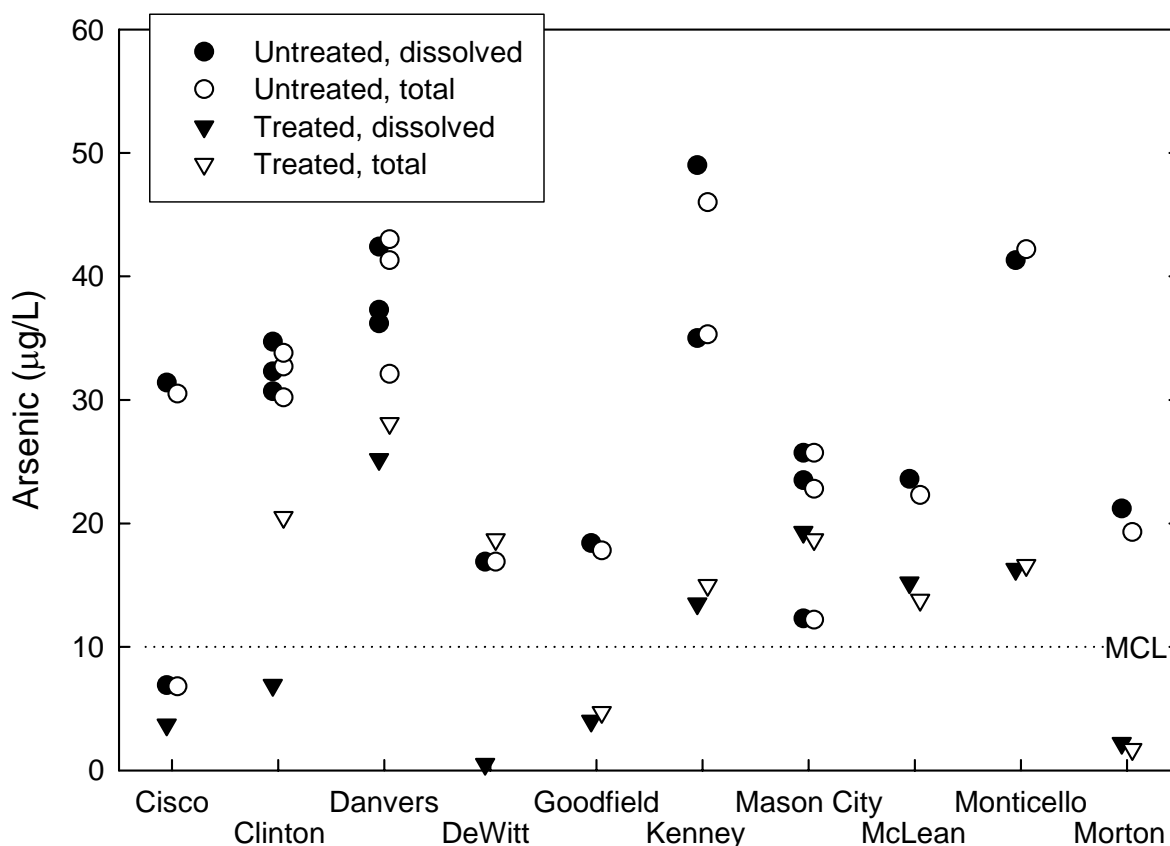
Figure 34. Comparison of dissolved (d) and total (t) arsenic concentrations in untreated and treated water at water treatment plants that use Mahomet Aquifer water. Dotted line is new maximum contaminant level for arsenic (10 Ϝg/L).

The Goodfield and Morton plants were the only ones that produced water with total arsenic concentrations less than the 10 μg/L MCL. The dissolved arsenic concentrations at the Clinton and DeWitt plants were below the MCL, but the total concentrations were greater than 20 μg/L. Improved filtration may allow these plants to meet the MCL. The water from the Cisco plant satisfied the MCL, but it is not known if that was because of effective treatment or because it had been using water from the well with the lower arsenic concentration. The dissolved and total arsenic concentrations in Mason City's treated water were between the minimum and maximum concentrations in the untreated waters, which is what would be expected for a mixture of those waters. There was no filtration and, therefore, no iron removal at Mason City (Table 15). As a result, there was no arsenic removal. The dissolved and total arsenic concentrations were nearly equal at Danvers, Goodfield, Kenney, McLean, Monticello, and Morton, so filtration was effective at those plants. The Cisco unfiltered sample was not analyzed due to a laboratory accident.

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There is some arsenic removal at water treatment plants that remove iron, although the degree of arsenic removal varies (MCNEILL and EDWARDS, 1995). Several factors affect As(V) sorption to hydrous ferric oxide (HFO), including the relative concentrations of arsenic and Fe, and the concentrations of competing ions, including phosphate (PO_4^{3-}), HCO_3^-, silica (SiO_2), and organic carbon (HOLM, 2002; REDMAN et al., 2002). Figure 35 compares arsenic removal with the concentrations of Fe, PO_4^{3-}, HCO_3^-, and SiO_2. Cisco was not considered because it was unclear what the input arsenic concentration was. For plants with two or three wells in operation, the median input values were used. All values are normalized to the maximum value and are arranged in decreasing efficiency of arsenic removal. There are few, if any, apparent trends. For example, the maximum arsenic removal was at the plant with the maximum Fe concentration, but the third best arsenic removal was at the plant with the minimum Fe. Phosphate competes with As(V) for HFO sorption sites, but the maximum arsenic removal was at the plant with the maximum PO_4^{3-} concentration.

Two or more factors may interact to affect arsenic removal. A simple linear model (equation 6) was fit to the community well data:

$$R = a_0 + a_1[As] + a_2[Fe] + a_3[PO_4^{3-}] + a_4[SiO_2] + a_5[Alk] + a_6[TOC] \qquad \textbf{(6)}$$

where R is percent removal, and a_0 ... a_6 are adjustable parameters. The model fit the data surprisingly well ($r^2=0.999$) with the largest residual (difference between observed and modeled values) being only 1%. The model parameters are given in Table 16. The goodness of fit is surprising because the interaction of some of the factors is expected to be nonlinear, e.g., the arsenic to iron ratio. Phosphate competes with arsenate for sorption to HFO, but the phosphate coefficient is positive. Clearly, more research is needed in this area.

Table 16. Parameters of a linear model of arsenic removal at water treatment plants.		
Component	*Parameter Value*	*Standard Error*
Constant	8.812	0.371
Dissolved arsenic concentration	-0.194	0.008
Iron concentration	-0.122	0.011
Phosphate concentration	1.764	0.143
Silica concentration	-1.420	0.063
Alkalinity	0.025	0.001
Total organic carbon concentration	-0.394	0.019
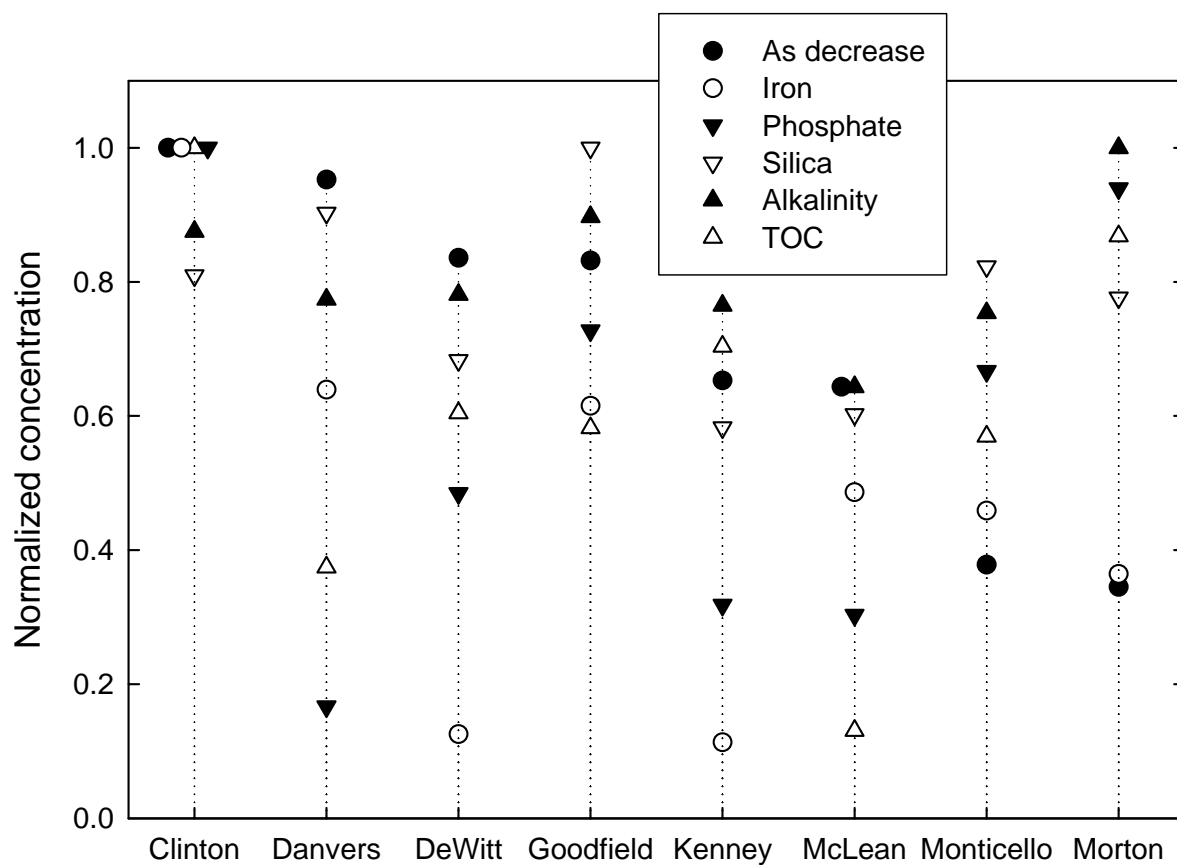
Figure 35. Arsenic removal at water treatment plants that use Mahomet Aquifer water
and concentrations of solutes that may affect arsenic removal.
All values are normalized to their maximum values.

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CONCLUSIONS

A robust, accurate analytical method based on HPLC and ICP-MS was developed for arsenic speciation. Good agreement between the sum of As(III) and As(V) concentrations in groundwater samples validated the method. Good recoveries of As(III) and As(V) spikes added to groundwater samples at the time of collection indicated that there were no significant changes in arsenic speciation between the time of sampling and analysis.

Arsenic concentrations between 10 and 50 Ғg/L were found in approximately 10% of the private wells sampled in Champaign County and in 35% of the wells in Tazewell County. Arsenic concentrations greater than 50 Ғg/L were found in approximately 10% of the Tazewell County wells and 2% (one well) of the Champaign County wells.

The areal distribution of arsenic in both Champaign and Tazewell Counties was complex. Wells with high (>50 Ғg/L) and low (<0.5 Ғg/L) concentrations were found less than 1 km apart. There were no significant differences in the average arsenic concentrations in the different depth classes in either Champaign or Tazewell County. The Glasford wells had the highest average concentration, but this may have been due to one well with an exceptionally high concentration.

The predominant arsenic species in most samples from private and public wells was As(III), although As(V) was detected in many samples. Methylated arsenic species were not detected in any samples. A small fraction (<10%) of the arsenic may be in particulate form (>0.45 Ғm). However, the particulate fraction is estimated from the difference between the arsenic concentrations in the unfiltered and filtered samples, so analytical precision limited our ability to measure particulate arsenic.

Arsenic speciation in Tazewell County was consistent with thermodynamic calculations based on the temperature, pH, and measured ORP values. Conversely, there was good agreement between redox potentials calculated from the temperature, pH, and arsenic speciation and measured ORP values. However, dissolved arsenic concentrations were unrelated to either pH or ORP values.

In Tazewell County there were no good correlations between arsenic concentrations and any other constituent. However, high arsenic concentrations tended to be associated with high values of alkalinity, TOC, and fluoride and with low concentrations of manganese and sulfate. In Champaign County, high arsenic concentrations were associated with high values of alkalinity, TOC, and ammonia nitrogen and low sulfate concentrations.

For raw water samples collected from water treatment plants, the total arsenic concentrations were all below 50 Ғg/L, as expected. All plants but one chlorinated their water, and As(V) was the only arsenic species detected in treated water from those plants. For the plant that did not chlorinate, the arsenic speciation was the same in raw and treated water. All treatment plants but one used some form of iron removal and there was some arsenic removal at all of those plants. There was no arsenic removal at the plant that did not remove iron.

Three water treatment plants produced water with less than 10 Fg/L arsenic. One plant had switched to new wells with very low arsenic concentrations and the other two had good arsenic removal. Five plants had between 10 and 20 Fg/L arsenic in their treated water. For two of those plants the dissolved arsenic concentration was below 10 Fg/L, so improved filtration may enable those plants to satisfy the new MCL. Process modifications may be needed at the other plants.

RECOMMENDATIONS FOR FURTHER RESEARCH

The combination of acidification with hydrochloric acid, keeping samples cold, and determining arsenic speciation within a day or two of sample collection avoided any oxidation or reduction of As(III)/As(V) spikes added to groundwater samples. Acidification was also necessary to prevent the precipitation of ferric oxide/hydroxide. It is unclear whether any factor was more important than the other two in preserving the arsenic speciation, but it is clear that the added chloride resulted in a higher (worse) ICP-MS arsenic detection limit because of ArCl formation. Sulfuric acid should be tested as a preservative for groundwater samples.

It was difficult to estimate the particulate or colloidal arsenic concentration from the difference between filtered and unfiltered water samples because of the combined uncertainty of sampling and analysis. Therefore, the particulate arsenic concentration should be determined by filtering a measured amount of water through a membrane filter and analyzing the filter. The capsule filters used in this project cannot be analyzed.

There are many private wells in the Glasford Aquifer and some of the highest arsenic concentrations were found in groundwater samples from this aquifer. The western part of the Mahomet Aquifer is known to have areas with high arsenic concentrations but the present study showed that the Mahomet Aquifer in Champaign County also has some areas with high arsenic. The Mahomet Aquifer is part of a larger continuous system, the Sankoty-Mahomet Aquifer. The Sankoty Aquifer extends northward through Tazewell, Woodford, Marshall, and Putnam Counties (WILSON et al., 1994). We recommend that the distribution and geochemistry of arsenic be characterized in: (1) the Glasford Aquifer; (2) the Mahomet Aquifer east and north of Champaign County; and (3) the Sankoty Aquifer.

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APPENDIX A

COMPLETE CHEMICAL RESULTS FOR DOMESTIC WELLS SAMPLED IN TAZEWELL COUNTY, CHAMPAIGN COUNTY, AND COMMUNITY WELLS

Arsenic concentrations reported in Ϝg/L, other parameters reported in mg/L unless specified otherwise. Alkalinity reported as $CaCO_3$. Nitrate and ammonia reported as N. Sulfate reported as SO_4.

Abbreviations:

  As, d = dissolved arsenic
  As, t = total arsenic (unfiltered sample)
  NA = not analyzed
  NS = no sample
  dup = duplicate sample

Tazewell County - Table A-1.
Champaign County - Table A-2.
Community Wells - Table A-3.

Table A-1. Complete chemical results for domestic wells sampled in Tazewell County.

Bottles	aq class	Depth (ft)	Date	Temp ($^\circ$C)	pH	ORP (mv)	SpC (μS cm^{-1})	DO
118	shallow	146	09/09/2002	13.5	7.31	61	629	0.38
119	Glasford	90	09/09/2002	13.7	6.87	133	968	0.34
120	Glasford	90	09/09/2002	13.7	6.87	133	968	0.34
121	medium	214	09/09/2002	14.0	7.22	70	819	0.31
122	GUB	106	09/09/2002	13.9	7.21	59	613	0.37
123	shallow	140	09/09/2002	15.0	7.41	43	676	0.33
124	deep	270	09/09/2002	14.6	7.45	29	647	0.43
125	medium	194	09/09/2002	13.9	7.39	51	612	0.50
126	medium	112	09/10/2002	16.4	7.18	125	567	0.48
127	deep	195	09/10/2002	13.5	7.22	50	603	0.40
128	Glasford	83	09/10/2002	13.9	7.14	276	571	0.85
129	Glasford	83	09/10/2002	13.9	7.14	276	571	0.85
130	shallow	104	09/10/2002	13.7	6.74	117	1352	0.40
131	shallow	187	09/10/2002	13.7	7.07	64	737	0.40
132	shallow	164	09/10/2002	16.1	6.93	174	845	0.37
133	deep	228	09/10/2002	14.8	7.2	81	585	0.42
134	medium	221	09/10/2002	14.0	7.17	101	645	0.38
135	deep	272	09/11/2002	15.4	7.27	6.3	702	0.40
136	shallow	167	09/09/2002	13.2	6.69	126	745	<0.55
137	medium	216	09/09/2002	21.0	7.17	54	810	<0.36
138	medium	216	09/09/2002	21.0	7.17	54	810	<0.36
139	medium	285	09/09/2002	14.8	7.39	38	641	<0.23
140	medium	304	09/09/2002	14.0	7.41	57	497	<0.17
142	deep	375	09/09/2002	13.3	7.55	52	857	<0.27
143	deep	347	09/09/2002	15.1	7.68	47	506	<0.19
144	shallow	279	09/10/2002	15.4	7.09	49	529	<0.27
145	shallow	279	09/10/2002	15.4	7.09	49	529	<0.27
146	shallow	209	09/10/2002	14.3	6.93	94	636	<0.23
148	medium	252	09/10/2002	12.8	7.04	86	684	<0.22
149	Glasford	176	09/10/2002	12.8	6.62	119	1070	<0.27
150	medium	246	09/10/2002	12.2	6.95	119	699	<0.36
151	deep	236	09/10/2002	15.9	7.27	39	823	<0.20
152	medium	273	09/11/2002	13.9	7.27	69	639	0.40
154	medium	197	09/11/2002	12.6	7.05	70	764	<0.43
155	medium	197	09/11/2002	12.6	7.05	70	764	<0.43
156	deep	220	09/11/2002	15.3	7.14	67	777	<0.32
158	Glasford	141	09/11/2002	13.3	6.69	121	799	<0.21
159	shallow	175	09/11/2002	14.6	7.06	77	743	<0.28
160	deep	295	09/11/2002	14.0	7.28	45	876	<0.24
161	deep	220	09/11/2002	12.9	7.34	60	647	0.30
162	deep	203	09/11/2002	13.1	7.33	55	718	0.30
163	deep	203	09/11/2002	13.1	7.33	55	718	0.30
164	medium	169	09/11/2002	13.7	7.19	59	773	0.23
165	deep	100	09/11/2002	13.3	7.49	35	683	0.23
166	medium	113	09/11/2002	14.9	7.26	67	646	0.29
167	deep	175	09/11/2002	12.9	7.31	80	583	0.36
168	deep	117	09/11/2002	13.3	7.03	98	765	0.29
172	deep	370	09/16/2002	13.2	7.21	63	880	<0.41
173	shallow	305	09/11/2002	14.5	7.26	52	912	<0.18
174	deep	370	09/16/2002	13.2	7.21	63	880	<0.41
175	medium	340	09/16/2002	12.9	7.29	57	839	<0.31
176	deep	163	09/16/2002	12.6	7.38	113	580	<0.32
177	medium	159	09/16/2002	13.2	7.44	48	726	<0.38
179	shallow	121	09/16/2002	13.3	7.37	73	728	<0.35

Table A-1 continued.

Bottles	As^{3+}	As^{5+}	As, d	As, t	Al	Na	Mg	Ca	Fe	Mn	Si	P	NH$_3$-N
118	3.24	0.798	4.19	4.07	0.002	6.08	33.9	78.0	1.99	0.052	8.93	0.106	0.746
119	1.31	0.554	1.61	2.24	0.002	24.2	45.4	140	2.60	0.809	6.34	<0.1	0.604
120	1.20	0.494	1.65	2.20	<0.002	23.4	45.6	150	2.47	0.805	6.70	<0.1	0.605
121	2.43	< 0.5	2.62	2.73	0.002	14.5	43.4	130	3.53	0.020	10.6	0.141	2.45
122	18.0	0.736	18.9	20.1	0.002	12.9	33.3	70.1	3.35	0.021	8.30	0.213	2.31
123	56.3	2.91	59.9	62.5	<0.002	34.2	35.7	59.5	1.62	0.050	7.30	<0.1	2.55
124	25.1	1.17	26.1	27.4	0.002	25.3	38.5	60.8	1.93	0.050	9.06	<0.1	0.773
125	92.0	5.97	94.0	100	<0.002	21.7	36.8	62.5	1.43	0.010	7.81	<0.1	1.96
126	0.650	< 0.5	0.594	1.31	<0.002	7.48	29.6	69.6	0.295	0.109	8.11	<0.1	0.274
127	3.09	< 0.5	3.16	3.51	0.002	10.7	32.0	71.4	3.26	0.166	10.3	<0.1	0.414
128	NA	NA	< 0.5	< 0.5	<0.002	7.18	30.5	72.0	<0.1	0.022	7.80	<0.1	0.035
129	NA	NA	< 0.5	< 0.5	<0.002	7.25	30.7	67.7	<0.1	0.022	7.67	<0.1	0.009
130	1.07	< 0.5	1.23	1.53	<0.002	19.5	72.9	170	3.86	0.349	7.51	<0.1	0.173
131	30.0	0.824	32.8	32.9	0.003	19.4	39.1	79.4	2.76	0.018	11.4	0.141	3.24
132	NA	NA	< 0.5	< 0.5	<0.002	11.2	44.4	100	0.309	0.263	7.81	<0.1	<0.03
133	NA	NA	< 0.5	< 0.5	<0.002	5.95	31.3	74.4	0.976	0.100	8.55	<0.1	<0.03
134	NA	NA	< 0.5	< 0.5	0.002	3.88	35.3	85.1	0.694	0.099	7.21	<0.1	<0.03
135	20.6	1.73	22.4	23.7	0.002	14.4	41.6	75.0	1.46	0.029	9.98	0.098	2.15
136	42.2	1.57	45.2	46.2	0.003	49.2	44.8	56.1	1.82	0.013	8.05	<0.1	1.60
137	73.7	4.69	80.6	82.1	0.002	52.8	39.9	69.2	3.45	0.016	11.7	<0.1	1.90
138	73.7	4.50	80.1	82.0	0.002	51.2	37.9	69.1	3.41	0.016	10.5	0.112	1.89
139	0.670	< 0.5	0.582	0.970	<0.002	13.6	33.6	74.2	2.35	0.086	8.32	<0.1	0.269
140	NA	NA	NA	< 0.5	0.002	5.46	25.3	59.7	1.06	0.096	7.64	<0.1	0.204
142	NA	NA	NA	< 0.5	<0.002	59.3	34.6	77.6	1.71	0.143	8.36	<0.1	0.581
143	NA	NA	NA	< 0.5	<0.002	5.92	26.2	64.2	1.06	0.159	7.89	<0.1	0.107
144	0.780	< 0.5	0.546	0.872	0.002	10.0	27.2	64.4	1.48	0.058	7.67	<0.1	0.479
145	0.858	< 0.5	0.690	0.872	0.002	10.1	28.4	68.5	1.45	0.058	7.66	<0.1	0.480
146	1.72	< 0.5	1.60	2.23	0.002	4.74	41.1	90.5	1.67	0.189	7.58	<0.1	0.085
148	NA	NA	< 0.5	< 0.5	<0.002	5.71	35.5	87.5	1.27	0.082	7.03	<0.1	0.165
149	180	7.00	190	200	0.002	51.2	47.1	97.8	3.49	0.026	11.2	0.123	14.6
150	NA	NA	< 0.5	< 0.5	<0.002	4.81	35.4	93.6	1.24	0.253	5.47	<0.1	<0.03
151	10.4	11.01	22.2	26.9	0.002	52.9	34.6	75.1	3.63	0.156	7.58	0.190	3.73
152	NA	NA	< 0.5	< 0.5	0.003	14.2	34.4	74.1	1.24	0.098	10.5	0.151	1.07
154	10.4	0.854	11.1	11.7	0.002	46.6	38.7	70.8	2.53	0.027	8.60	0.181	3.18
155	10.3	1.16	11.0	11.8	0.002	46.6	38.9	71.2	2.51	0.027	8.72	0.188	3.21
156	10.8	< 0.5	11.0	11.6	0.002	53.0	41.2	76.1	2.92	0.031	8.76	0.194	3.27
158	82.8	5.65	92.6	NS	0.002	18.5	46.1	90.3	3.55	0.019	11.4	<0.1	7.27
159	27.1	1.09	28.7	29.4	0.002	39.3	37.5	72.0	2.43	0.020	8.65	0.134	3.18
160	0.856	< 0.5	0.902	1.11	0.002	85.6	43.2	80.0	3.86	0.065	9.51	0.187	3.45
161	20.1	1.05	20.9	22.2	0.002	18.3	36.1	71.3	1.80	0.035	8.14	0.135	1.67
162	55.4	1.41	56.1	58.7	0.002	24.7	41.2	76.2	2.70	0.020	10.9	0.164	2.53
163	54.5	1.70	56.6	59.7	0.002	24.0	41.0	74.0	2.56	0.021	11.1	0.154	2.61
164	21.2	9.60	32.5	44.0	0.002	23.6	41.3	84.4	3.40	0.019	12.2	0.192	3.65
165	14.2	1.22	15.1	15.8	0.002	17.1	34.9	68.3	1.83	0.032	8.23	0.158	1.64
166	NA	NA	< 0.5	< 0.5	<0.002	4.17	35.2	81.2	2.02	0.097	7.65	<0.1	0.123
167	0.578	0.510	0.500	0.488	0.002	3.42	30.8	72.9	1.71	0.118	7.39	<0.1	0.080
168	5.32	0.54	5.70	6.08	0.003	7.75	41.8	98.3	2.62	0.110	8.23	<0.1	0.142
172	6.37	0.564	7.11	7.80	0.002	71.9	45.5	90.2	3.18	0.048	10.2	0.230	3.07
173	9.99	< 0.5	11.4	11.7	0.002	91.7	33.7	64.6	2.48	0.041	8.60	0.241	4.00
174	5.88	< 0.5	7.10	7.41	0.002	63.7	40.0	81.5	2.99	0.043	9.96	0.240	3.09
175	6.22	< 0.5	6.82	6.81	0.002	60.8	39.6	77.4	3.55	0.050	9.24	0.225	2.84
176	NA	NA	< 0.5	< 0.5	<0.002	2.26	33.7	74.5	0.496	0.428	9.05	<0.1	0.133
177	57.1	2.15	64.8	64.7	0.002	24.8	41.4	73.2	3.68	0.017	11.2	0.136	2.36
179	13.5	< 0.5	15.4	15.6	0.002	24.4	35.3	78.5	3.22	0.027	11.4	0.171	3.92

Table A-1 concluded.

Bottles	alkalinity	lab pH	HCO₃	F	Cl	NO₃-N	SO₄	PO₄	TOC
118	311	7.58	379	0.266	7.60	<0.06	41.8	< 0.25	1.18
119	325	7.18	396	< 0.25	71.2	<0.06	120	< 0.25	0.80
120	325	7.18	396	< 0.25	71.9	<0.06	120	< 0.25	0.70
121	473	7.46	577	0.326	2.10	<0.06	< 0.25	< 0.25	2.44
122	355	7.53	433	0.339	0.919	<0.06	< 0.25	< 0.25	2.18
123	391	7.77	477	0.565	1.98	0.406	3.82	< 0.25	5.04
124	377	7.83	459	0.329	1.09	<0.06	< 0.25	< 0.25	2.63
125	360	7.83	439	0.377	0.846	<0.06	< 0.25	< 0.25	2.97
126	283	7.45	345	0.313	6.23	1.66	28.1	< 0.25	0.70
127	338	7.53	413	0.323	3.75	<0.06	< 0.25	< 0.25	1.00
128	256	7.52	312	0.300	7.23	3.08	48.4	< 0.25	0.50
129	256	7.53	312	0.300	7.20	2.99	48.0	< 0.25	0.50
130	422	7.15	515	0.262	66.9	<0.06	290	< 0.25	1.11
131	432	7.45	526	0.337	2.06	<0.06	< 0.25	< 0.25	3.61
132	360	7.35	438	0.260	39.8	0.177	68.9	< 0.25	0.60
133	298	7.54	363	0.284	3.77	<0.06	44.5	< 0.25	0.50
134	304	7.65	371	0.279	5.56	<0.06	66.9	< 0.25	0.40
135	406	7.49	495	0.338	1.13	<0.06	< 0.25	< 0.25	2.53
136	441	7.67	538	0.378	3.14	<0.06	< 0.25	< 0.25	4.47
137	467	7.70	569	0.337	2.96	<0.06	< 0.25	< 0.25	5.81
138	467	7.73	570	0.339	2.91	<0.06	< 0.25	< 0.25	5.94
139	375	7.80	457	< 0.25	1.19	<0.06	< 0.25	< 0.25	1.80
140	289	7.81	352	< 0.25	0.650	<0.06	< 0.25	< 0.25	0.70
142	456	7.78	556	0.266	30.0	<0.06	< 0.25	< 0.25	5.73
143	294	7.86	358	< 0.25	0.839	<0.06	0.427	< 0.25	0.80
144	309	7.76	377	0.308	0.992	<0.06	< 0.25	< 0.25	1.29
145	309	7.78	377	0.300	0.953	<0.06	< 0.25	< 0.25	1.34
146	323	7.63	394	0.278	2.95	<0.06	48.9	< 0.25	0.70
148	353	7.69	430	0.293	3.66	0.061	48.4	< 0.25	0.80
149	637	7.27	777	0.509	2.70	<0.06	< 0.25	< 0.25	13.0
150	333	7.57	406	0.257	11.7	<0.06	60.8	< 0.25	0.60
151	432	7.73	526	0.489	28.5	0.140	2.78	< 0.25	5.88
152	363	7.46	443	0.341	3.02	<0.06	< 0.25	< 0.25	1.68
154	421	7.75	514	0.460	13.5	<0.06	< 0.25	< 0.25	4.64
155	423	7.66	516	0.460	15.9	<0.06	< 0.25	< 0.25	5.03
156	420	7.67	512	0.461	13.6	<0.06	< 0.25	< 0.25	5.28
158	461	7.37	562	0.449	1.16	<0.06	< 0.25	< 0.25	5.02
159	404	7.73	493	0.452	13.6	<0.06	< 0.25	< 0.25	4.17
160	450	7.70	549	0.449	32.5	<0.06	< 0.25	< 0.25	6.02
161	370	7.49	452	0.384	3.02	<0.06	< 0.25	< 0.25	2.04
162	406	7.48	496	0.384	3.74	<0.06	< 0.25	< 0.25	2.79
163	406	7.45	495	0.426	3.90	<0.06	< 0.25	< 0.25	2.71
164	438	7.33	534	0.386	3.19	<0.06	< 0.25	< 0.25	3.50
165	265	7.47	323	0.388	42.8	<0.06	42.2	< 0.25	1.73
166	267	7.30	325	0.295	7.56	<0.06	88.3	< 0.25	0.50
167	235	7.56	287	0.292	7.48	<0.06	77.4	< 0.25	0.40
168	357	7.34	435	0.302	11.8	<0.06	59.7	< 0.25	0.40
172	502	7.46	613	0.442	4.79	<0.06	< 0.25	< 0.25	7.91
173	461	7.72	562	0.454	39.3	<0.06	< 0.25	< 0.25	6.84
174	504	7.53	615	0.421	4.40	<0.06	< 0.25	< 0.25	7.88
175	474	7.62	578	0.440	7.70	<0.06	< 0.25	< 0.25	6.72
176	325	7.62	397	0.263	1.55	<0.06	7.88	< 0.25	0.60
177	414	7.57	505	0.381	3.19	<0.06	< 0.25	< 0.25	3.64
179	399	7.55	487	0.373	10.1	<0.06	< 0.25	< 0.25	3.20

Table A-2. Complete chemical results for domestic wells sampled in Champaign County.

Bottles	aq class	Depth (ft)	Date	Temp (EC)	pH	ORP (mv)	SpC (F S cm^{-1})	DO
58	deep	266	06/18/2002	14.10	7.13	67	784	0.21
59	shallow	189	06/18/2002	13.50	6.93	130	776	0.27
60	medium	220	06/19/2002	12.80	6.75	110	663	0.51
61	medium	270	06/20/2002	13.30	7.13	69	685	0.39
62	medium	270	06/18/2002	13.30	7.13	69	685	0.39
64	deep	255	06/18/2002	14.00	6.88	130	712	0.33
65	shallow	218	06/18/2002	13.20	6.77	119	666	0.29
66	shallow	202	06/18/2002	15.80	7.00	104	690	0.17
67	Glasford	87	06/19/2002	13.00	6.66	140	844	0.86
68	Glasford	80?	06/19/2002	12.10	6.73	124	709	0.56
69	medium	300	06/19/2002	13.10	6.54	135	1085	0.70
70	medium	240	06/26/2002	13.74	7.54	33	711	0.35
71	shallow	207	06/26/2002	14.24	7.39	78	708	0.38
72	shallow	207	06/26/2002	14.24	7.39	78	708	0.38
73	Glasford	92	06/19/2002	12.80	6.87	109	622	0.70
74	Glasford	92	06/19/2002	12.80	6.87	109	622	0.70
75	medium	220	06/19/2002	12.90	6.82	116	642	0.40
76	deep	303	06/19/2002	13.10	6.94	87	662	0.64
77	medium	227	06/19/2002	13.15	7.35	74	675	0.40
78	shallow	200	06/18/2002	14.12	7.49	37	636	0.28
79	medium	230	06/19/2002	13.77	7.09	80	889	0.44
80	medium	318	06/19/2002	13.91	7.37	43	635	0.53
81	medium	220	06/18/2002	13.42	7.59	45	632	0.34
82	deep	312	06/19/2002	13.60	7.55	38	593	0.39
83	deep	312	06/19/2002	13.60	7.55	38	593	0.39
84	deep	300+	06/19/2002	14.27	7.64	31	635	0.47
86	deep	255?	06/20/2002	13.71	7.11	54	730	0.33
87	deep	260	06/18/2002	14.53	7.84	14	558	0.59
88	medium	201	06/18/2002	12.80	7.30	63	697	0.40
89	medium	225	06/18/2002	13.21	7.39	51	695	0.31
90	shallow	165	06/18/2002	12.78	7.03	62	754	0.33
91	shallow	165	06/18/2002	12.78	7.03	62	754	0.33
92	Glasford	100?	06/18/2002	12.92	6.93	93	804	0.37
93	medium	223	06/18/2002	13.65	7.36	58	668	0.26
94	medium	250	06/18/2002	13.64	7.53	50	687	0.72
95	shallow	240	06/18/2002	13.60	7.48	43	686	0.30
96	deep	303	06/18/2002	13.93	7.61	46	684	0.38
97	shallow	180	06/26/2002	14.43	7.26	67	715	0.46
102	Glasford	75	06/20/2002	14.56	6.85	101	1080	0.41
104	shallow	258	06/26/2002	14.14	7.18	97	724	0.37
107	shallow	220	06/26/2002	13.72	7.05	65	887	0.50
108	shallow	198	06/26/2002	13.47	6.93	89	800	0.30
109	medium	280+	06/26/2002	13.60	7.07	44	802	0.30
110	shallow	210	06/26/2002	13.87	6.75	132	850	0.46
111	medium	250	06/26/2002	13.52	6.86	122	905	0.50
112	medium	250	06/26/2002	13.52	6.86	122	905	0.50
113	Glasford	87	06/26/2002	14.19	6.81	128	815	0.42
114	Glasford	157	06/26/2002	15.71	6.85	84	818	0.42
115	shallow	200	06/26/2002	13.34	6.95	89	849	0.43
170	Glasford	135	10/09/2002	12.60	7.09	102	737	0.41
180	deep	275+	10/09/2002	14.50	7.18	94	699	---
182	deep	309	10/09/2002	13.38	7.46	89	684	0.41
183	deep	309	10/09/2002	13.38	7.46	89	684	0.41
184	deep	335	10/09/2002	13.73	7.46	60	623	0.51
185	medium	279	10/09/2002	14.30	7.45	61	597	0.39

Table A-2 continued.

Bottles	As^{3+}	As^{5+}	As, d	As, t	Al	Na	Mg	Ca	Fe	Mn	Si	P	NH$_3$-N
58	NA	NA	NA	< 1	0.001	45.0	35.2	77.0	3.04	0.024	8.22	0.222	2.02
59	NA	NA	NA	< 1	<0.001	18.0	37.5	89.8	2.72	0.038	9.85	0.191	1.06
60	NA	NA	NA	< 1	0.001	25.1	33.4	79.3	2.19	0.025	9.60	0.293	1.60
61	NA	NA	NA	< 1	0.001	10.3	17.2	42.2	1.69	0.017	9.57	0.243	1.64
62	NA	NA	NA	< 1	<0.001	18.2	37.1	93.6	1.77	0.038	9.74	0.194	1.05
64	NA	NA	NA	< 1	0.001	23.4	35.9	76.9	1.74	0.037	9.96	0.164	1.39
65	< 1	< 1	< 1	1.1	0.001	17.5	34.6	75.6	1.59	0.029	10.3	0.134	1.13
66	NA	NA	NA	< 1	<0.001	20.6	33.6	77.2	1.62	0.031	9.64	0.145	1.04
67	NA	NA	NA	< 1	<0.001	7.72	48.6	100	2.61	0.181	6.21	<0.04	<0.03
68	NA	NA	NA	< 1	<0.001	6.90	39.9	83.9	2.08	0.040	8.21	<0.04	0.11
69	1.5	< 1	1.4	2.1	<0.001	14.6	71.2	120	4.48	0.073	9.90	0.161	0.80
70	4.2	< 1	4.7	5.3	0.001	36.2	34.5	60.2	2.78	0.036	6.67	0.109	1.07
71	NA	NA	NA	< 1	0.002	19.0	32.3	74.9	1.85	0.026	9.44	0.248	1.66
72	NA	NA	NA	< 1	0.004	18.3	31.8	73.9	2.01	0.027	9.49	0.247	1.68
73	2.3	< 1	1.9	2.1	0.001	24.1	29.8	72.0	2.51	0.029	9.57	0.143	0.74
74	2.2	< 1	1.7	2.2	<0.001	23.7	30.1	74.4	2.36	0.028	9.76	0.137	0.75
75	2.1	< 1	1.7	2.1	<0.001	25.4	31.2	79.2	2.43	0.027	10.0	0.119	0.79
76	2.1	< 1	1.7	2.0	0.001	17.4	33.6	80.5	2.27	0.015	9.28	0.217	1.54
77	6.6	1.3	8.0	9.0	0.001	12.1	17.4	42.3	1.75	0.018	9.11	0.134	1.23
78	5.7	< 1	5.8	6.2	<0.001	33.0	30.5	58.7	1.74	0.018	7.41	0.239	1.15
79	NA	NA	NA	< 1	<0.001	10.1	25.3	51.8	2.33	0.046	7.08	0.054	0.22
80	NA	NA	NA	< 1	0.001	16.8	18.0	33.5	1.60	0.047	7.26	0.095	1.22
81	1.6	< 1	1.2	1.3	0.001	32.0	31.5	55.9	1.30	0.049	6.82	0.080	0.68
82	3.5	< 1	2.9	3.8	0.001	35.4	32.4	52.6	2.14	0.052	6.72	<0.04	1.12
83	3.5	< 1	2.9	3.8	0.002	36.5	33.0	52.0	2.33	0.052	6.58	0.040	1.12
84	2.8	< 1	2.4	3.1	0.001	16.8	18.1	30.7	1.61	0.032	5.80	0.067	0.85
86	NA	NA	NA	< 1	0.001	11.7	18.6	45.8	2.04	0.074	9.32	0.195	1.21
87	9.9	< 1	9.7	11	<0.001	56.1	22.7	40.1	1.23	0.015	5.36	0.095	0.26
88	3.9	< 1	4.2	4.7	<0.001	22.6	30.7	79.3	2.61	0.021	9.32	0.193	1.18
89	4.8	< 1	5.2	6.8	<0.001	18.1	30.0	76.7	2.90	0.021	9.04	0.172	1.19
90	19	< 1	20	26	0.001	11.6	33.8	79.2	5.79	0.042	11.2	0.442	5.76
91	20	< 1	21	24	<0.001	12.1	34.7	84.3	5.91	0.040	11.2	0.446	5.82
92	45	2.0	50	53	0.001	18.6	38.9	79.4	4.40	0.037	9.77	0.378	7.97
93	NA	NA	NA	< 1	0.001	18.0	32.0	72.0	1.49	0.017	8.67	0.231	2.65
94	< 1	< 1	< 1	1.3	<0.001	31.3	30.8	65.9	1.66	0.024	7.75	0.197	1.80
95	NA	NA	NA	< 1	<0.001	30.1	31.4	71.5	1.53	0.018	7.52	0.210	1.75
96	1.6	< 1	1.9	2.3	0.001	35.3	32.9	65.2	1.40	0.022	7.26	0.140	1.09
97	4.7	< 1	5.6	7.0	0.001	23.9	30.8	73.5	1.83	0.016	9.24	0.138	1.23
102	2.6	< 1	2.3	3.0	0.001	11.9	31.9	60.9	2.45	0.079	7.68	0.062	0.15
104	NA	NA	NA	< 1	0.002	31.4	31.1	73.7	1.65	0.023	11.2	0.097	0.94
107	14	< 1	16	17	0.001	35.0	33.2	77.4	2.93	0.039	8.00	0.570	2.92
108	< 1	< 1	< 1	1.1	0.001	20.5	30.4	74.2	2.37	0.039	9.32	0.328	1.59
109	3.7	< 1	3.5	3.9	0.001	21.2	31.0	78.4	3.11	0.034	9.44	0.193	1.27
110	NA	NA	NA	< 1	0.002	28.6	37.9	82.2	1.84	0.046	11.4	0.075	0.86
111	NA	NA	NA	< 1	0.001	27.2	38.1	83.9	2.36	0.034	10.4	0.136	1.39
112	NA	NA	NA	< 1	0.001	26.9	36.7	83.9	2.14	0.033	10.7	0.146	1.33
113	NA	NA	NA	< 1	0.002	17.0	33.2	79.0	2.05	0.031	10.7	0.093	1.51
114	1.6	< 1	2.1	2.5	0.001	22.2	34.7	80.7	3.57	0.049	9.40	0.387	1.83
115	2.5	< 1	2.6	2.6	0.001	22.6	31.0	85.5	3.01	0.022	9.43	0.276	0.98
170	12.8	1.4	13.7	15.3	<0.002	10.0	39.0	93.0	2.20	0.068	10.0	<0.1	0.75
180	< 0.5	0.7	0.5	0.5	<0.002	25.0	34.0	82.0	1.30	0.025	10.0	0.180	1.28
182	1.4	1.1	2.0	1.9	0.002	28.0	37.0	74.0	0.350	0.019	7.80	0.120	1.82
183	1.3	1.2	1.7	2.1	<0.002	28.0	37.0	74.0	0.400	0.018	8.00	0.120	1.81
184	3.4	0.6	3.6	3.7	<0.002	31.0	35.0	60.0	1.40	0.034	7.40	<0.1	1.33
185	0.7	0.6	0.7	0.7	<0.002	24.0	36.0	62.0	1.34	0.039	8.00	<0.1	1.30

Table A-2 concluded.

Bottles	alkalinity	lab pH	HCO_3	F	Cl	NO_3-N	SO_4	PO_4	TOC
58	373		455	0.515	1.8	<0.06	65	0.608	4.4
59	390		475	0.38	1.5	<0.06	48	<0.25	1.9
60	374		456	0.42	0.69	<0.06	<0.25	0.64	2.5
61	356		434	0.46	0.94	0.587	5.8	0.37	2
62	390		476	0.42	1.5	<0.06	48	<0.25	1.8
64	373		455	0.47	0.81	<0.06	29	<0.25	2.2
65	380		463	0.46	0.63	<0.06	<0.25	<0.25	2
66	355		433	0.61	4.9	0.101	21	<0.25	2.3
67	377		460	<0.25	14	<0.06	77	<0.25	1
68	371		452	<0.25	2.3	<0.06	26	<0.25	0.89
69	387		472	<0.25	17	<0.06	200	<0.25	1.4
70	369		450	<0.25	2	<0.06	1.5	0.45	2.2
71	376		459	<0.25	0.77	<0.06	<0.25	<0.25	2.4
72	378		461	<0.25	0.76	<0.06	<0.25	0.42	2.5
73	328		400	0.28	0.67	<0.06	19	<0.25	1.4
74	326		397	0.29	0.66	<0.06	20	<0.25	1.6
75	338		413	0.28	0.7	<0.06	18	<0.25	1.8
76	372		453	<0.25	0.45	<0.06	0.27	0.48	1.8
77	342		418	0.32	0.96	<0.06	23	<0.25	1.7
78	343		418	0.27	1.7	<0.06	<0.25	<0.25	2.4
79	327		399	<0.25	51	<0.06	69	<0.25	1.1
80	353		430	0.26	1.1	<0.06	<0.25	<0.25	1.7
81	349		425	<0.25	1.7	<0.06	<0.25	0.37	2.2
82	323		393	0.27	1.9	<0.06	<0.25	<0.25	2
83	326		398	0.27	1.9	<0.06	<0.25	<0.25	2.2
84	341		415	<0.25	1.2	<0.06	<0.25	<0.25	1.6
86	373		455	<0.25	0.99	<0.06	17	<0.25	2
87	299		364	0.31	2.9	<0.06	<0.25	<0.25	3.1
88	335		409	0.25	1.1	<0.06	39	<0.25	2
89	345		421	0.28	0.99	<0.06	22	<0.25	1.8
90	386		471	0.31	4.2	<0.06	<0.25	<0.25	4.4
91	392		478	0.31	4.3	0.079	<0.25	<0.25	4.4
92	422		515	0.48	2.7	0.074	<0.25	0.33	4.5
93	361		440	0.33	0.94	<0.06	0.85	<0.25	3.1
94	372		454	0.31	1.4	<0.06	<0.25	<0.25	2.7
95	381		465	0.29	1.3	<0.06	0.39	<0.25	3.1
96	374		456	0.29	1.7	<0.06	<0.25	<0.25	2.4
97	345		421	<0.25	1.3	<0.06	23	<0.25	1.9
102	359		438	<0.25	55.0	<0.06	141.9	<0.25	1.3
104	380		463	0.26	1.3	<0.06	<0.25	<0.25	2.9
107	395		482	<0.25	1.2	0.092	0.41	0.52	3.1
108	352		429	<0.25	0.75	<0.06	0.4	<0.25	2
109	345		421	<0.25	0.83	<0.06	5	<0.25	1.8
110	382		466	<0.25	0.68	<0.06	0.74	<0.25	1.9
111	375		457	<0.25	1.1	<0.06	28	<0.25	1.8
112	373		455	<0.25	1	<0.06	28	<0.25	2
113	363		442	0.27	0.72	<0.06	0.4	<0.25	2.6
114	377		460	<0.25	0.63	0.076	<0.25	<0.25	2
115	380		464	<0.25	0.71	<0.06	0.4	<0.25	2.4
170	347	7.38	423	0.36	12	<0.06	47	< 0.25	1.5
180	345	7.55	421	0.35	1.0	<0.06	45	< 0.25	1.5
182	382	7.77	466	0.38	0.82	<0.06	2.8	< 0.25	1.8
183	384	7.76	468	0.39	0.80	<0.06	2.7	< 0.25	1.8
184	348	7.78	425	0.37	1.1	<0.06	< 0.25	< 0.25	1.7
185	341	7.75	416	0.38	0.79	<0.06	< 0.25	< 0.25	1.2

Table A-3. Complete chemical results for community wells sampled.

Location	County	Well #	Type	Bottles	Date	Temp (EC)	pH	ORP (mv)	SpC (FS cm⁻¹)	DO
Cisco	Piatt	3	Raw	31	03/08/2002	13.5	8.20	99	950	<5.3
Cisco	Piatt	4	Raw	33	03/08/2002	13.5	8.47	67	975	<0.39
Cisco	Piatt	3,4	Finished	36X	03/08/2002	NA	NA	NA	NA	NA
Clinton	DeWitt	6	Raw	30	03/13/2002	13.34	7.23	116	894	<0.24
Clinton	DeWitt	8	Raw	29	03/13/2002	13.68	7.20	143	904	<0.36
Clinton	DeWitt	10	Raw	28	03/13/2002	12.86	7.22	<281	887	<0.45
Clinton	DeWitt	6,8,10	Finished	53	03/13/2002	16.0	7.07	679	886	1.55
Danvers	McLean	3	Raw	11	03/07/2002	11.8	8.92	78	1348	<0.52
Danvers	McLean	4	Raw	12	03/07/2002	NA	NA	NA	NA	NA
Danvers	McLean	5	Raw	13	03/07/2002	NA	NA	NA	NA	NA
Danvers	McLean	5	Finished	15	03/07/2002	NA	NA	NA	NA	NA
DeWitt	DeWitt	1	Raw	4	03/08/2002	NA	6.92	114	1254	<0.35
DeWitt	DeWitt	1	Finished	5	03/08/2002	NA	6.64	681	1247	<0.20
Goodfield	Woodford	1	Raw	20	03/08/2002	12.9	8.27	71	1162	<0.31
Goodfield	Woodford	1	Finished	35	03/08/2002	13.3	5.41	716	1154	6.36
Kenney	DeWitt	1	Raw	26	03/13/2002	13.23	7.35	<95	878	<0.30
Kenney	DeWitt	1	Finished	27	03/13/2002	9.81	7.50	910	941	7.19
Mason City	Mason	3	Raw	10	03/13/2002	13.2	7.05	<76	555	<0.50
Mason City	Mason	4	Raw	22	03/13/2002	13.17	7.15	126	492	<0.55
Mason City	Mason	5	Raw	25	03/13/2002	13.91	7.18	<190	507	<0.33
Mason City	Mason	3,4,5	Finished	24	03/13/2002	14.38	7.04	>638	523	0.5
McLean	McLean	3	Raw	7	03/08/2002	13.32	7.00	98	981	<0.25
McLean	McLean	3	Finished	8	03/08/2002	13.78	7.20	268	993	4.23
Monticello	Piatt	4	Raw	1	03/07/2002	14.06	7.42	63	607	0.42
Monticello	Piatt	4	Finished	2	03/07/2002	12.48	7.49	944	630	9.36
Morton	Tazewell	3	Raw	18	03/08/2002	13.3	8.45	66	990	<2.8
Morton	Tazewell	4	Raw	17	03/08/2002	NA	NA	NA	NA	NA
Morton	Tazewell	6	Raw	19	03/08/2002	11.9	8.40	68	1106	<1.3
Morton	Tazewell	6	Finished	36	03/08/2002	NA	NA	NA	NA	NA
Rantoul	Champaign	5	Raw	41	03/13/2002	13.1	7.62	NA	816.7	<1.34
Rantoul	Champaign	8	Raw	44	03/13/2002	12.9	7.57	181	871	<1.59
Rantoul	Champaign	9	Raw	47	03/13/2002	12.8	7.52	264	802	<0.70
Rantoul	Champaign	12	Raw	46	03/13/2002	13.5	7.55	190	766	<0.90
Rantoul	Champaign		Finished	42	03/13/2002	17.9	7.79	NA	552.4	8.16

Table A-3 continued.

Location	Bottles	As^{3+}	As^{5+}	As, d	As, t	Al	Na	Mg	Ca	Fe	Mn	Si
Cisco	31	26.7	1.87	31.39	30.5	0.001	34.0	38.1	72.7	3.60	0.017	9.71
Cisco	33	6.56	< 2	6.946	6.75	0.001	42.0	36.6	80.5	2.77	0.031	7.55
Cisco	36X	< 2	4.74	3.678	NA	<0.001	170	12.0	34.0	0.053	0.006	8.41
Clinton	30	31.2	< 2	32.3	32.7	<0.001	92.7	36.2	68.9	0.732	0.018	6.60
Clinton	29	30.8	< 2	34.7	33.8	<0.001	93.7	36.7	70.2	0.723	0.018	6.55
Clinton	28	29.6	< 2	30.7	30.2	0.001	96.6	32.9	65.3	1.81	0.020	6.95
Clinton	53	< 2	7.60	6.88	20.5	<0.001	95.3	33.3	64.0	0.200	0.017	6.47
Danvers	11	32.8	6.19	37.3	43.0	0.001	220	22.7	52.4	1.53	0.021	6.88
Danvers	12	37.4	3.76	42.4	32.1	<0.001	130	35.1	75.8	2.99	0.034	8.14
Danvers	13	32.6	5.63	36.2	41.3	0.001	165	32.3	69.3	2.12	0.029	7.72
Danvers	15	< 2	24.5	25.2	28.1	0.000	160	37.1	57.5	0.065	0.032	7.91
DeWitt	4	15.3	< 2	16.9	16.9	0.001	210	29.0	65.0	5.82	0.043	7.82
DeWitt	5	< 2	< 2	< 1	18.7	0.001	200	30.1	65.6	0.210	0.032	7.57
Goodfield	20	16.7	< 2	18.4	17.8	0.001	85.0	37.2	73.9	3.59	0.095	9.66
Goodfield	35	< 2	4.10	4.01	4.66	0.001	91.0	37.8	73.5	0.222	0.081	8.96
Kenney	26	35.5	1.99	35.0	35.3	0.001	84.5	36.1	66.8	0.657	0.016	5.63
Kenney	27	< 2	16.3	13.5	15.0	<0.001	110	38.6	67.2	<0.02	<0.002	5.66
Mason City	10	23.5	3.80	25.7	25.7	<0.001	6.87	33.9	70.9	0.647	0.256	8.54
Mason City	22	9.25	4.27	12.3	12.2	0.001	5.26	30.0	71.5	0.123	0.211	9.88
Mason City	25	14.5	8.86	23.5	22.8	0.001	6.37	30.7	66.8	0.525	0.227	10.5
Mason City	24	< 2	21.5	19.3	18.7	<0.001	6.62	33.1	69.6	0.298	0.194	9.17
McLean	7	22.0	< 2	23.6	22.3	0.001	125	31.4	67.0	2.67	0.036	7.95
McLean	8	11.8	2.49	15.2	13.8	0.004	130	30.8	65.1	0.184	0.038	8.12
Monticello	1	36.6	2.52	41.3	42.2	<0.001	40.0	31.6	64.1	2.83	0.064	5.82
Monticello	2	< 2	14.9	16.3	16.6	0.002	110	18.0	38.0	0.082	<0.002	5.84
Morton	18	17.9	< 2	17.8	16.7	0.003	47.0	40.7	71.0	3.80	0.032	8.72
Morton	17	21.4	< 2	19.0	22.1	0.001	47.0	42.2	74.0	3.72	0.032	8.25
Morton	19	18.8	< 2	21.2	19.3	0.002	52.0	41.6	70.9	3.33	0.021	9.02
Morton	36	< 2	< 2	2.21	1.68	0.002	160	13.0	26.0	0.028	0.025	8.53
Rantoul	41	< 2	< 2	< 1	< 1	0.003	28.4	31.3	83.2	2.35	0.034	8.37
Rantoul	44	< 2	< 2	< 1	< 1	<0.001	39.1	32.4	76.8	2.09	0.048	7.58
Rantoul	47	< 2	< 2	< 1	< 1	<0.001	29.8	30.5	80.0	0.325	0.031	7.87
Rantoul	46	< 2	< 2	< 1	< 1	<0.001	25.4	29.7	74.7	2.42	0.026	8.04
Rantoul	42	< 2	< 2	< 1	< 1	0.703	35.6	21.0	41.0	0.138	0.004	5.44

Table A-3 concluded.

| Location	Bottles	P	F	Cl	NO$_3$-N	SO$_4$	PO$_4$	TOC	NH$_3$-N	alkalinity	HCO$_3$	lab pH
Cisco	31	0.412	0.357	7.15	0.025	0.15	0.1	4.95	6.33	401	489	7.26
Cisco	33	0.334	0.309	16.7	< 0.02	2.30	< 0.1	3.33	2.56	401	489	7.37
Cisco	36X	0.038	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Clinton	30	0.303	0.608	46.4	< 0.02	< 0.1	0.104	9.64	3.72	434	529	7.44
Clinton	29	0.322	0.592	50.9	< 0.02	< 0.1	0.124	9.19	3.02	425	519	7.46
Clinton	28	0.402	0.730	50.1	< 0.02	< 0.1	0.206	9.04	3.31	417	508	7.65
Clinton	53	0.031	0.960	60.0	0.129	0.231	< 0.1	13.3	2.44	389	475	7.16
Danvers	11	0.623	0.324	48.9	< 0.02	< 0.1	1.12	13.2	7.12	495	603	7.48
Danvers	12	0.691	0.330	29.1	< 0.02	< 0.1	0.366	13.2	9.40	556	678	7.46
Danvers	13	0.509	0.312	41.0	< 0.02	< 0.1	0.351	13.4	8.29	544	663	7.44
Danvers	15	0.131	0.838	39.3	< 0.02	< 0.1	0.382	12.8	8.35	531	647	7.59
DeWitt	4	0.657	0.551	130	< 0.02	< 0.1	0.134	15.2	5.57	476	580	7.37
DeWitt	5	0.031	0.763	140	0.045	< 0.1	< 0.1	9.14	5.08	478	583	7.32
Goodfield	20	0.476	0.340	16.1	< 0.02	< 0.1	< 0.1	8.85	4.62	488	595	7.31
Goodfield	35	0.045	1.03	33.9	0.241	< 0.1	0.132	8.58	3.33	447	545	7.23
Kenney	26	0.214	0.423	48.2	< 0.02	< 0.1	< 0.1	10.7	2.65	416	507	7.50
Kenney	27	0.110	0.494	73.5	0.034	0.235	0.265	9.02	0.06	409	498	7.60
Mason City	10	1.49	0.121	3.47	0.429	30.8	0.229	2.70	0.63	272	331	7.09
Mason City	22	0.942	0.115	1.33	1.118	12.0	0.316	1.18	0.20	266	324	7.12
Mason City	25	1.84	0.124	2.51	0.362	13.8	0.660	0.90	0.58	275	335	7.19
Mason City	24	1.02	1.01	4.31	0.827	20.0	0.275	0.80	0.22	269	328	7.11
McLean	7	0.446	0.409	73.9	< 0.02	< 0.1	0.178	8.66	4.49	410	500	7.80
McLean	8	0.092	1.31	73.6	< 0.02	< 0.1	0.209	9.37	4.47	422	515	7.35
Monticello	1	0.195	0.242	4.17	< 0.02	0.840	< 0.2	1.99	0.82	350	427	7.73
Monticello	2	0.575	0.828	12.2	0.043	0.845	1.17	2.08	<0.03	330	403	7.76
Morton	18	0.121	0.333	10.5	< 0.02	< 0.1	< 0.1	5.69	2.88	421	513	7.50
Morton	17	0.067	0.327	9.85	< 0.02	< 0.1	< 0.1	5.55	2.91	430	524	7.40
Morton	19	0.112	0.333	14.1	< 0.02	< 0.1	< 0.1	5.85	2.99	420	512	7.46
Morton	36	<0.02	0.908	20.9	0.118	0.250	< 0.1	5.08	1.55	410	500	7.59
Rantoul	41	0.179	0.162	0.62	< 0.02	0.426	< 0.1	1.10	1.81	369	450	7.50
Rantoul	44	0.613	0.194	0.92	< 0.02	2.18	0.368	4.73	3.11	382	466	7.42
Rantoul	47	0.038	0.159	1.02	< 0.02	0.603	< 0.1	4.08	1.76	358	436	7.46
Rantoul	46	0.160	0.173	0.78	< 0.02	< 0.1	< 0.1	6.38	1.75	339	414	7.36
Rantoul	42	0.994	1.17	9.01	0.410	8.42	0.695	1.73	1.43	233	284	8.49

APPENDIX B

**ADDITIONAL GRAPHS SHOWING RELATIONSHIPS BETWEEN DISSOLVED
ARSENIC AND OTHER CHEMICAL PARAMETERS FOR DOMESTIC WELLS
SAMPLED IN TAZEWELL AND CHAMPAIGN COUNTIES AND COMMUNITY
WELLS IN THE MAHOMET AQUIFER**
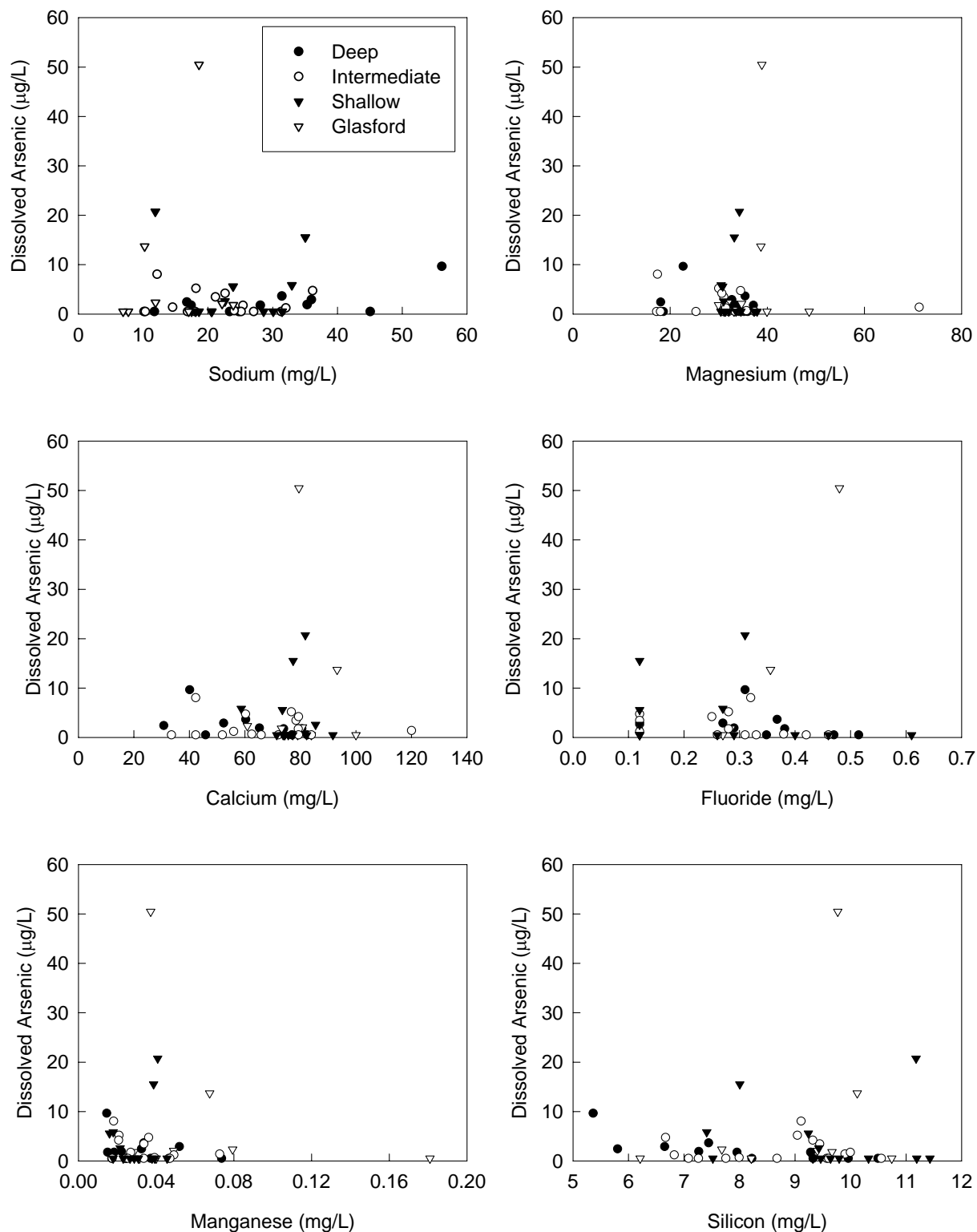
Tazewell County - Figure B-1.
Champaign County - Figures B-2 and B-3.
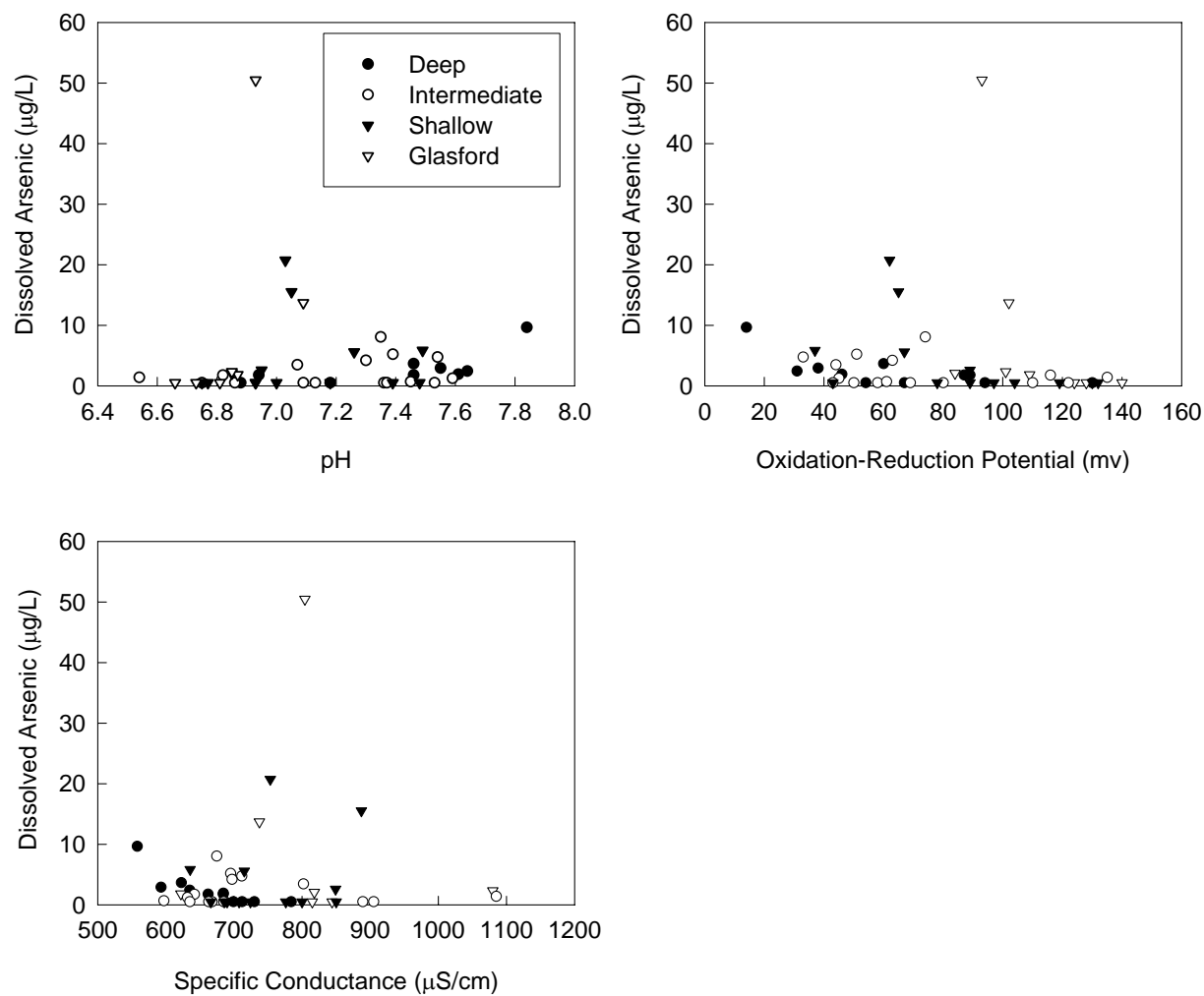Community Wells - Figures B-4 and B-5.
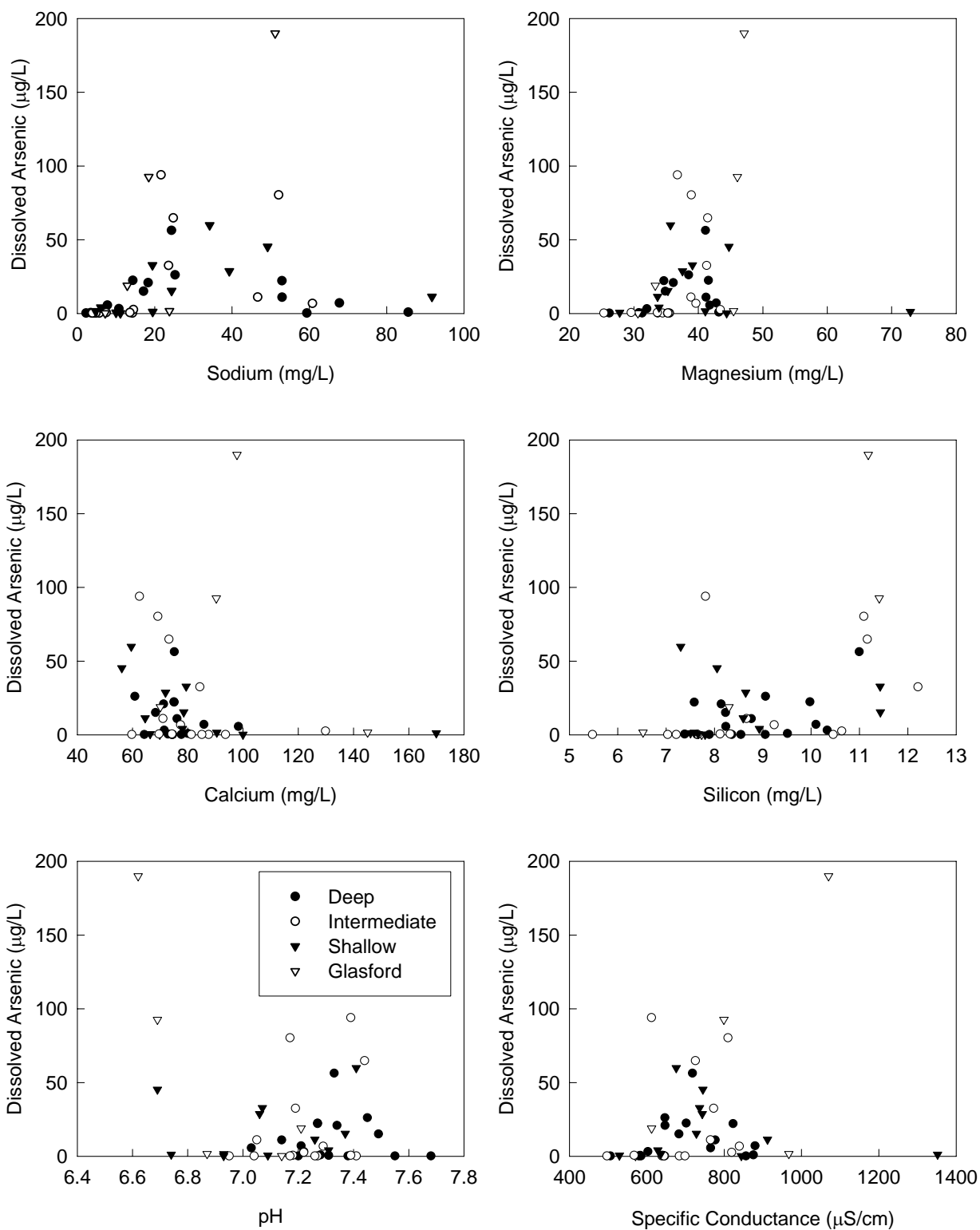
Figure B-1. Dissolved arsenic versus sodium, magnesium, calcium, silica, pH, and specific conductance for samples collected from private wells in Tazewell County.
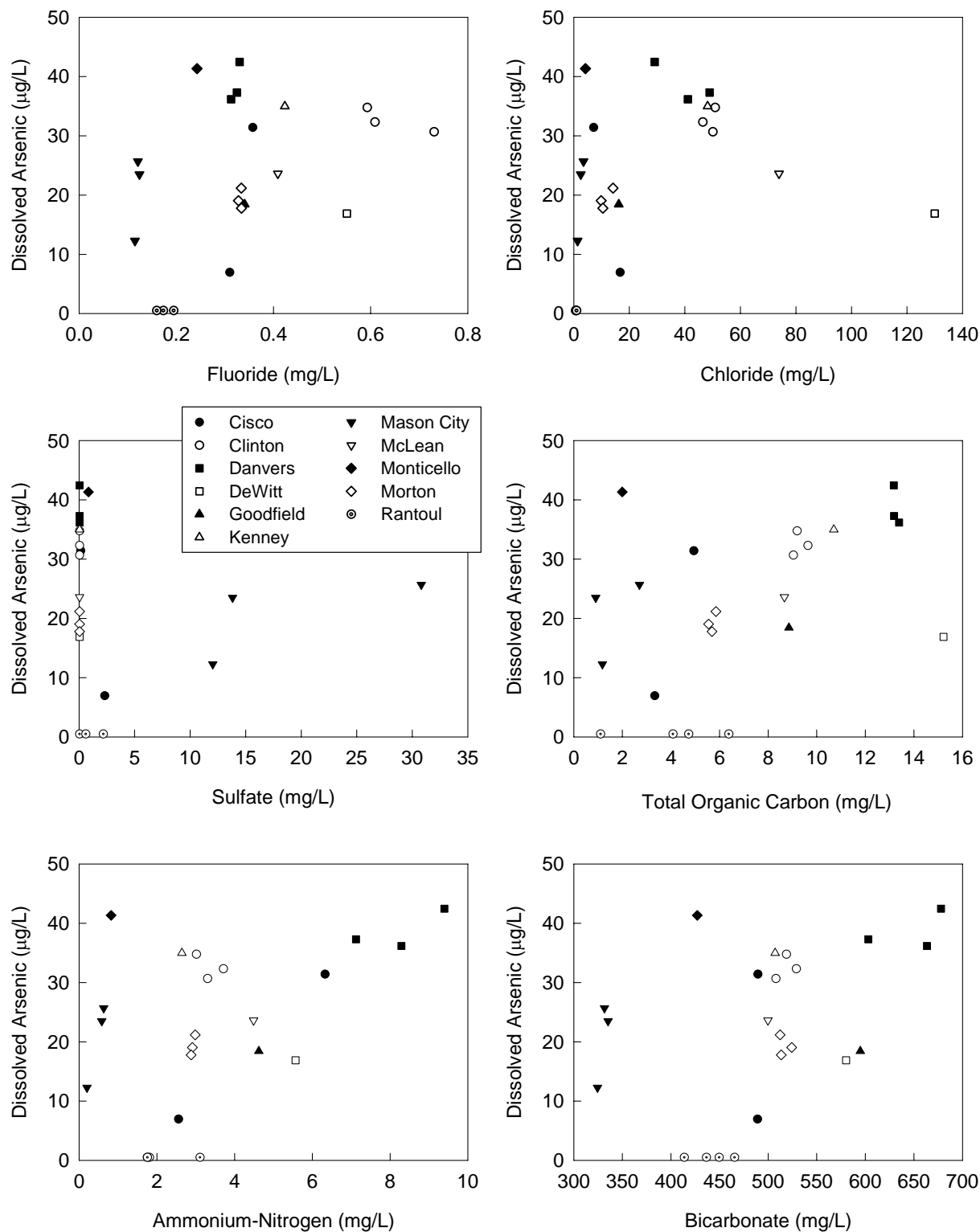
Figure B-2. Dissolved arsenic versus sodium, magnesium, calcium, fluoride, manganese, and silica for samples collected from private wells in Champaign County.

Figure B-3. Dissolved arsenic versus pH, ORP, and specific conductance for samples collected from private wells in Champaign County.

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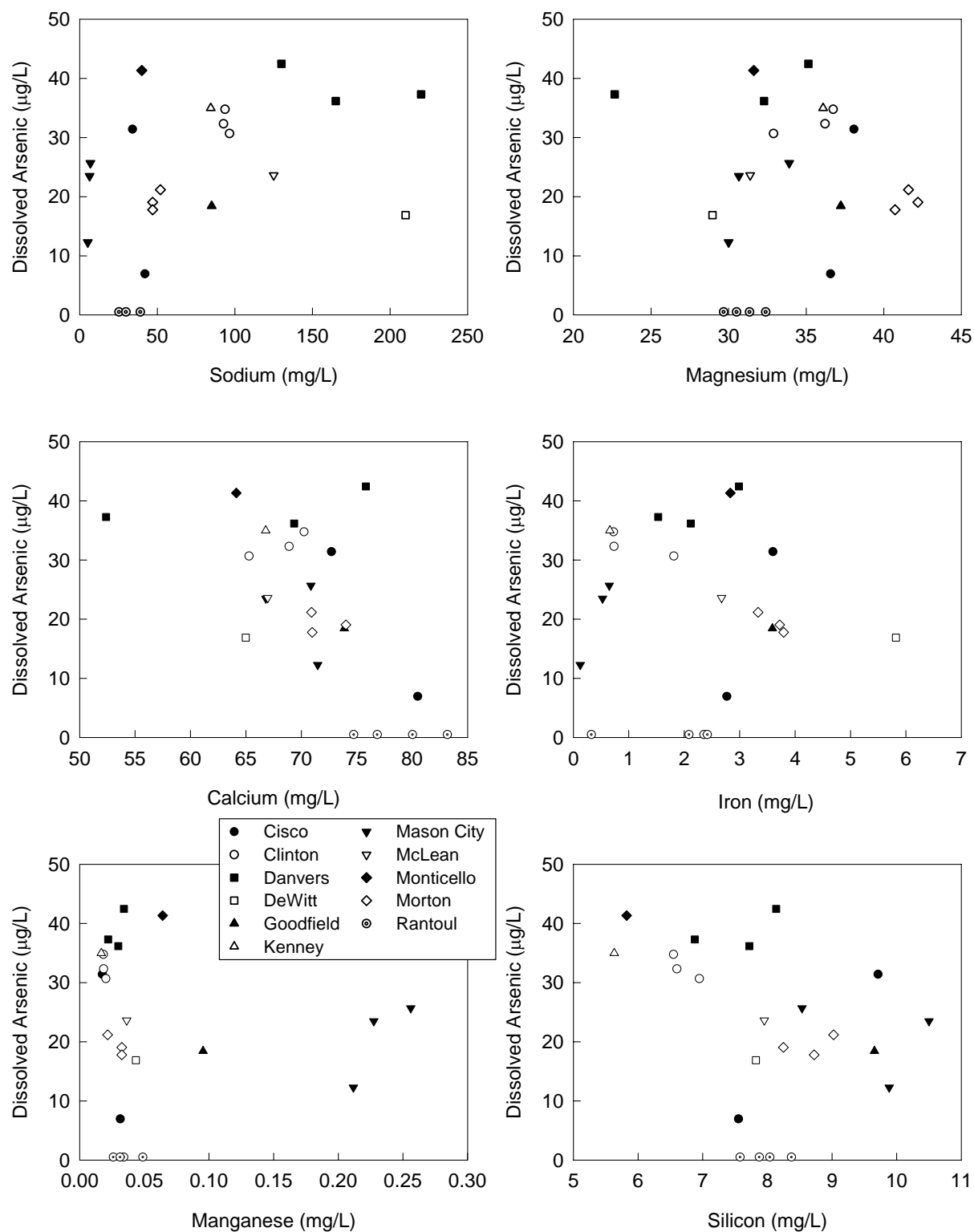
Figure B-4. Dissolved arsenic versus sodium, magnesium, calcium, iron, manganese, and silica for raw water samples collected from community wells in the Mahomet Aquifer.

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Figure B-5. Dissolved arsenic versus fluoride, chloride, sulfate, TOC, ammonium-N, and bicarbonate for raw water samples collected from community wells in the Mahomet Aquifer.

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